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Appl. No. : 09/943,217
Filed : August 29, 2001

REMARKS

Claim 1 has been amended. Claims 1-15 are now pending in this application. Support for the amendments is found in the existing claims and the specification as discussed below.

Accordingly, the amendments do not constitute the addition of new matter. Applicant respectfully requests the entry of the amendments and reconsideration of the application in view of the amendments and the following remarks.

Rejection under 35 U.S.C. § 103(a)

Claims 1-15 are rejected under 35 U.S.C. § 103(a) as being unpatentable over the Tan article in Macromolecules or the Tan article in ACS Preprints or CN 1257885 in view of Stevens '415.

The Examiner asserts that each of the primary references polymerize polycarbonate from carbon dioxide and propylene oxide using a catalyst which is a combination of Yttriumtrihaloacetate, diethyl zinc and glycerol. The references lack ethylene or propylene carbonate. However, Stevens '415 is cited for teaching that propylene carbonate produced as a by-product can be recycled and the Examiner asserts that upon recycling, the 3-part catalyst of the primary references becomes a 4-part catalyst.

In response to Applicants' arguments, the Examiner asserts that there is no evidence that the carbonate functions as a catalyst or raises the activity of the catalysts. The Examiner also states that claim 1 does not require any specific combining steps and continues to assert that it would have been obvious to recycle the propylene carbonate by-product back into the feed which would result in the 4-part catalyst of Applicants' claims.

Applicants have amended claim 1 in order to clarify the claimed subject matter. In response to the Examiner's comment that claim 1 does not require any specific combining steps, claim 1 has been amended to recite that the carbonate is obtained by stirring or grinding said mixture, and then aging it for 1-24 hours under 0-50 times atmospheric pressure of nitrogen, argon, carbon dioxide or under super critical condition. Support for this amendment is found in claim 9, for example. Claim 1 has also been amended to specify the type of polycarbonate which is an alternating copolymer having a content of alternative sequence structure of at least 95%. Support for the claim amendments is found within the claims and specification. See page 2, paragraph 0006 and page 5, paragraph 0027 of the specification. Claim 1 has also been amended

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to change the word "dependently" to --independently--. Support for this amendment is found in claim 9.

Applicants assert that the 4 components of the catalyst as claimed can be thoroughly mingled which differs from the teachings of the cited references, alone or in combination. Merely recycling of this propylene carbonate by-product back into the feed for the purpose of improving yield as suggested by the Examiner will not result in Applicants' claimed 4-part catalyst. Claim 1 has been amended to specify the process steps to distinguish the claimed invention from the combination of references cited by the Examiner. As now set forth in claim 1, the 4 components of the catalyst must be stirred or ground and then aged. Recycling of the propylene carbonate by-product in the presence of a 3-part catalyst is insufficient.

As discussed in the present specification, an object of the present application is to provide a catalyst for preparing high molecular weight polycarbonate. Molecular weight and content of the alternative sequences structure are two major factors determining the properties of the alternating polycarbonate. The object of the present invention is to provide a catalyst for preparing a polycarbonate having both improved average molecular weight and improved content of alternative sequence structure. Propylene carbonate or ethylene carbonate are incorporated into the 4-part catalyst system to improve the coordination of monomers to the active center which improves properties of the catalyst such as activity. A further object of the invention is to provide a catalyst for preparing desired polycarbonates without using any solvent. Attachment A is submitted in order to provide background to the Examiner on the field of alternating polycarbonates.

None of the primary references teach or suggest Applicants' invention as they are all drawn to a 3-part catalyst. Although the Examiner cites Stevens '415 to correct the deficiencies of the primary references, the Stevens '415 reference fails to do so. Stevens '415 relates to a polycarbonate having an average molecular weight of 700-5000 as a polyether carbonate of low molecular weight. Applicants refer the Examiner to attached Tables 1 & 2 (Attachment B) which compares the teaching of the cited references (Tan in Table 1 and Stevens in Table 2) with the claimed invention.

Furthermore, the polycarbonate of Stevens '415 is a block copolymer which differs from the alternating copolymer as presently claimed by Applicants. As is well known to the Examiner, the polycarbonate of Stevens '415 is a block copolymer which can be completely solubilized in

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methanol, and, in contrast, the polycarbonate obtained by using the present catalyst is an alternating polycarbonate which cannot be solubilized in methanol at all. In the present application, the block polycarbonate in the Stevens '415 form (block copolymer) has been completely removed by terminating the polymeric reaction using 5% HCl / methanol to completely precipitate the polymer and the resulting precipitate has been solubilized in methyl chloride followed by reprecipitating in methanol (an international standard for purifying alternating polycarbonates). Therefore, in Applicants' system, propylene carbonate and ethylene carbonate cannot be used to improve the yield of the alternating polycarbonate (see articles of Soga, K.; Vogdanis, L.; Lee, JC, in Attachment A). It has been shown that propylene carbonate or ethylene carbonate can never polymerize with itself or copolymerize with other epoxides to form an alternating polycarbonate with a high content of alternative sequence structure. Thus, the block polymers of Stevens '415 cannot be combined with the alternating copolymers of Applicants so there is no motivation to combine the disclosure of Stevens '415 with the teachings of any of the primary references. Stevens '415 does not relate to a method of producing an alternating copolymer having a content of alternative sequence structure of at least 95% as presently claimed.

Furthermore, in arguments the Examiner has focused on increased yield and has stated that "the data of record does not prove the presence of the carbonate increased yield" (Paper No. 09292003, page 3). However, Applicants wish to emphasize that the function of the propylene carbonate or ethylene carbonate is to improve the activity, not the yield. The activity of the catalyst is quite different from the yield (degree of utilization of the monomer). For example, with a conventional catalyst having a certain activity, it can be expected that the yield will be improved by recycling the propylene carbonate by-product back into the feed, but it does not follow that the catalyst activity and the molecular weight of the polymer will also be improved by the same method.

In the present application, propylene carbonate or ethylene carbonate plays a big role in forming a catalytic active center. In the examples shown in the description, the highest catalytic activity is 8.0×10^4 g/mol catalyst (examples 1 and 4) and the lowest is 4.61×10^4 g/mol catalyst (example 3). However, the activity in CN 1257885 is only 2.5×10^4 g/mol catalyst, and in the Tan article (Macromolecules 1997) it is only 4200 g/mol Y. In example 2 of the present application, the 4-parts catalyst system has an activity of 5.37×10^4 g/mol Y which is much

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higher than reported by Tan (Macromolecules 1997, 4200 g/mol Y). Therefore, clearly the carbonate component of the catalyst as claimed plays an important role in forming a catalytic active center onto which the monomers can be better coordinated. This clearly shows that the carbonate component functions as part of the catalyst.

Stevens '415 does not disclose any method for obtaining a polycarbonate of high molecular weight. Indeed Stevens '415 teach much lower molecular weights of 700-5000 (see col. 1, lines 19-21). Actually, a polymer of molecular weight 700-5000 would be considered in the art to be an oligomer rather than a high polymer. A distinguishing feature of the high molecular weight polymer of the presently claimed invention is that it has a specific glass transition temperature while an oligomer does not have a specific glass transition temperature. Furthermore, according to Stevens '415 the polycarbonate obtained is an intermediate which is useful for reaction with other compounds (see Stevens '415, col. 1, lines 45-65) while the polycarbonate obtained by the catalyst as presently claimed can be singly used as packaging or blocking materials.

Stevens '415 does not pertain to an alternating polycarbonate as presently claimed. Stevens '415 relates to a block polycarbonate having a low molecular weight which is a polyether carbonate while the presently claimed invention relates to an alternating polycarbonate (an alternating copolymer of carbon dioxide and epoxide). It is well known to those of ordinary skill in the art that the polyether carbonate of low molecular weight is a specific type of polycarbonate with a different structure and application from the alternating polycarbonates of the presently claimed invention.

The presently claimed invention is directed towards a high molecular weight polycarbonate which has a content of alternate sequence structure of at least 95%. This is quite different from the low molecular weight polycarbonate oligomers taught by Stevens '415. Additionally, Applicants teach the addition of propylene carbonate or ethylene carbonate to facilitate coordination of monomers to the active centers and thus to improve the properties of the catalyst such as activity.

The polycarbonate of Stevens '415 is a block polymer which is completely soluble in methanol. In contrast, the polycarbonate obtained using the present catalyst is an alternating polycarbonate which is insoluble in methanol. In the present application, the block polycarbonate in the Stevens '415 form (block copolymer) has been completely removed by

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terminating the polymeric reaction using 5% HCl/methanol to completely precipitate the polymer and solubilizing the resulting precipitation by methyl chloride followed by re-precipitating with methanol. It has been shown that the propylene carbonate or ethylene carbonate can never polymerize with itself or copolymerize with other epoxides to form an alternating polycarbonate of a high content of alternative sequence structure. Thus, Stevens '415 is not pertinent to the present invention because Stevens '415 does not teach alternating copolymers having a content of alternative sequence structure of at least 95%.

Finally, Stevens '415 does not teach or suggest a method of obtaining a catalyst for producing an alternating polycarbonate without using any solvent.

As is well-known, a prima facie case of obviousness requires that three basic criteria be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second there must be a reasonable expectation of success. Finally, the prior art reference (or references when combined) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed invention and the reasonable expectation of success must both be found in the prior art, and must not be based on Applicants' disclosure. In this case, there is no suggestion or motivation to combine Stevens '415 with any of the primary references and there is not a reasonable expectation of success.

It was not predictable at the time of the claimed invention that the recycled carbonate of Stevens '415 could interact synergistically with the 3-component catalyst of the primary reference to significantly raise the activity of the catalyst. Stevens '415 merely teaches recycling of a propylene bicarbonate by-product, not actively combining a rare earth coordination compound with an alkyl metal compound and a polyol and a carbonate following by aging. Even when Stevens '415 is combined with the primary references, there is no motivation for actively combining the 3 component system of the primary references with the by-product of Stevens '415. And even if one of ordinary skill in the art did combine the teachings of the primary references with the teaching of Stevens '415, one would not have reasonably expected that the carbonate would act catalytically. One of ordinary skill in the art would not have reasonably expected that the recycled carbonate could be incorporated into a three component system to obtain a 4 parts catalyst which can be used for producing a high molecular weight alternating polycarbonate without using any solvent. Thus, there was no motivation to combine Stevens

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'415 with the primary references and, once combined, there was no reasonable expectation of success.

In any case, the cited references, alone or in combination, fail to teach the method steps recited in claim 9. For example, step (a) recites that the 4 components are sequentially combined with the carbonate. This is followed by stirring or grinding the mixture in step (b), which is followed by aging the mixture in step (c). The cited references do not teach these method steps.

Furthermore, even if a prima facie case has been established (and Applicants maintain that it has not), the improved results reported by Applicants due to the synergistic effects of the addition of carbonate to the three component system disclosed by the primary references could not have been predicted by the cited references taken alone or in combination.

In order to facilitate a better understanding of the advantages of the present application, Applicants have carefully compared the features of the present invention to features of the cited references and the results are attached as Tables 1 and 2 (Attachment B).

In view of Applicants' amendments and arguments, reconsideration and withdrawal of this ground of rejection is respectfully requested.

CONCLUSION

In view of Applicants' amendments to the claims and the foregoing Remarks, it is respectfully submitted that the present application is in condition for allowance. Should the Examiner have any remaining concerns which might prevent the prompt allowance of the application, the Examiner is respectfully invited to contact the undersigned at the telephone number appearing below.

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Please charge any additional fees, including any fees for additional extension of time, or credit overpayment to Deposit Account No. 11-1410.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: Jan. 6, 2004

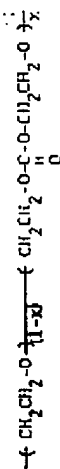
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NEW TYPE OF POLYMERIZATION OF ETHYLENE CARBONATE

It has been reported in the patent literature (1) that ethylene carbonate (EC) polymerizes at high temperature under the influence of some inorganic alkaline compounds to give a viscous polycarbonate having a molecular weight of 700-5000 and containing less than 15 wt-% CO_2 .

On the other hand, Sakai et al. (2) have obtained a white solid polycarbonate having a molecular weight of 5000-40,000 and containing as much as 30.6 wt-% CO_2 from the polymerization of EC at 150°C for 80 hr using $(\text{C}_4\text{H}_9)_3\text{Sn}(\text{OCH}_3)$ or $\text{Bu}_2\text{SnOC}_4\text{H}_9\text{O}$ as a catalyst. Judging from the CO_2 contents, these polymers can be considered to have the following structure, where the maximum value of x is 0.79 (at 30.6 wt-% CO_2).



In this article, we wish to report a new type of polymerization of EC (shown below) using $\text{Al}(\text{acac})_3$ or $\text{Ti}(\text{OBu})_4$ as a catalyst.



Polymerizations were carried out in a 50-ml stainless steel autoclave, usually without any solvent. Measured quantities of EC and catalyst were placed in the autoclave. The autoclave was degassed in vacuo and then kept standing in an oil bath equipped with a temperature regulator. After the reaction, the unreacted EC was removed by washing with diethyl ether, and the precipitate was adequately washed with hydrochloric acid - methanol and dried in vacuo at room temperature.

The composition of the polymer was mainly determined by use of a 100-MHz Jeol NMR spectrometer.

The specific viscosity of a 1% solution in chloroform was measured at 25°C with an Ubbelohde-type viscometer.

Table I presents the analytical data of the polymerizations with various catalysts, these indicate that such compounds as $\text{Al}(\text{acac})_3$ and $\text{Ti}(\text{OBu})_4$ have a specific catalytic property related to this new type of EC polymerization.

Hence, polymerizations were carried out in detail using $\text{Al}(\text{acac})_3$ as a catalyst.

The polymer produced was a pale-yellow viscous material soluble in chloroform, acetone, cyclohexanone, dimethyl formamide, dioxane, tetrahydrofuran, dimethylsulfoxide, etc., and insoluble in methanol, diethyl ether, benzene, toluene, n-hex., o-dichlorobenzene, etc.

TABLE I

Polymerizations of EC with Various Catalysts

Run No	EC (g)	Cat. ^a	Temp. (°C)	Period (hrs)	Yield (mg)	Conv. (%)	η_{inh}^c (dl/g)
01	2.0	no	140	93	0	0	0
02	1.0	Al(acac) ₃	150	140	324	32.4	96.2
03	1.0	Cr(acac) ₃	130	48	0	0	0
04	1.0	Co(acac) ₃	130	48	0	0	0
05	1.0	Fe(acac) ₃	150	60	0	0	0
06	1.0	Mn(acac) ₃	150	60	0	0	0
07	1.0	Mn(acac) ₃	150	60	0	0	0
08	1.0	MoO ₂ (acac) ₂	150	75	0	0	0
12	2.0	Zn(acac) ₂	150	75	trace ^b	trace	29.6
16	2.0	AlCl ₃	160	73	0	0	0
34	2.0	TiCl ₄	140	92	498 ^b	24.9	18.0
23	2.0	ZnCl ₂	175	92	0	0	0
15	2.0	Al(O- <i>i</i> Pr) ₃	160	73	0	0	0
25	2.0	Ti(ORu) ₄	130	72	380	19.0	95.2
29	2.0	Sn(Ph) ₃ Cl	140	96	6	0	0
37	3.0	(n-Bu ₃ Sn) ₂ O	175	90	320	10.7	70.0
40	3.0	ZnEt ₂ /Al ₂ O ₃	190	116	469 ^d	15.6	20.6

^aCa. 40 mg.^bMethanol-soluble polymer. The others are insoluble in methanol.^cThe content of $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{OCO}-$ linkage by assuming thestructure as $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{OCO}-\text{CH}_2\text{CH}_2-\text{O}-\text{C}-\text{O}-$ ^dIn CHCl₃ at 25°C.

Figures 1 and 2 show typical infrared and NMR spectra of the polymer.

The infrared spectrum displays strong characteristic absorption peaks at near 1745, 1250-1300, and 1100-1150 cm⁻¹, which are attributable to the carbonyl and carbonyl-oxygen stretching of carbonate linkage, and the carbon-oxygen stretching of ether linkage, respectively.

The NMR spectrum exhibits two characteristic peaks at $\delta = 4.31$ ppm and 3.75 ppm whose intensity ratio is just unity. These peaks can be assigned to methylene protons (a) and (b) in $-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$, respectively. (b) (a) (a) (b)

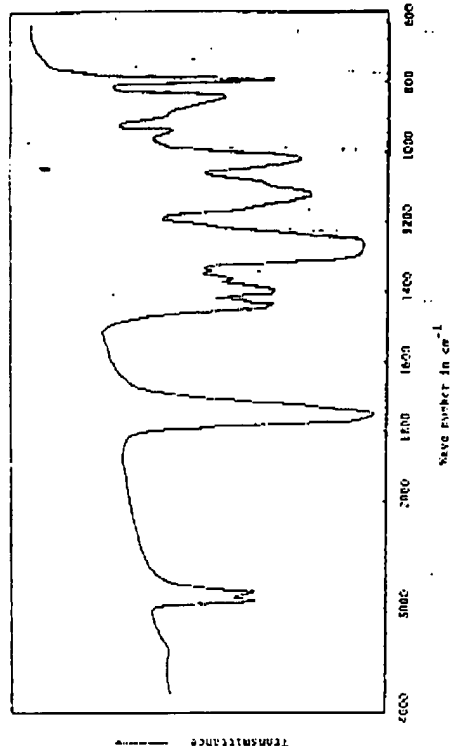


Fig. 1. IR spectrum of the polymer (run no. 09).

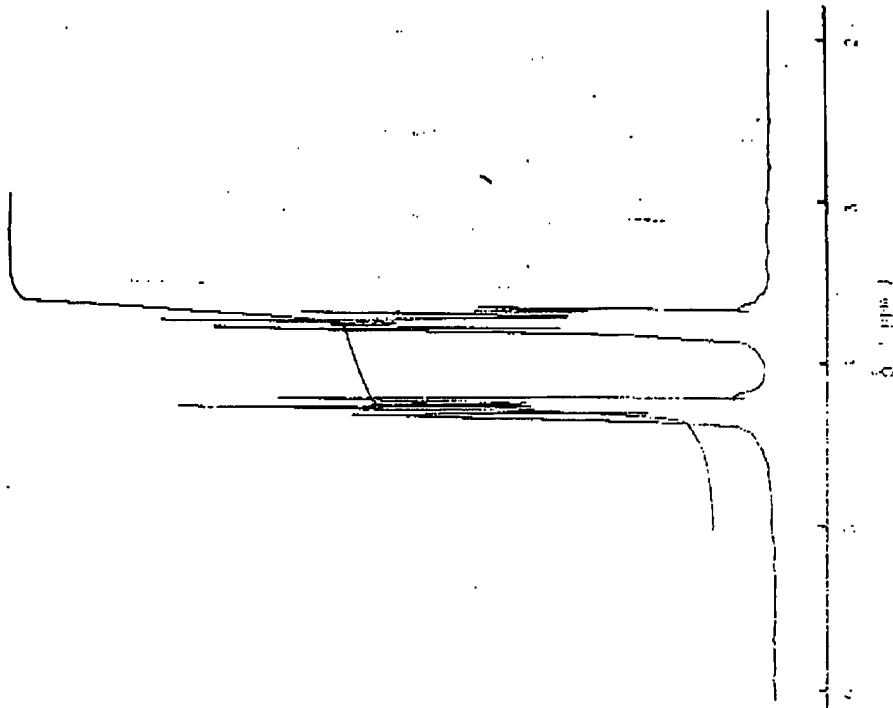


Fig. 2. NMR spectrum of the polymer (run no. 09).

Synthetic and thermodynamic investigations in the polymerization of ethylene carbonate

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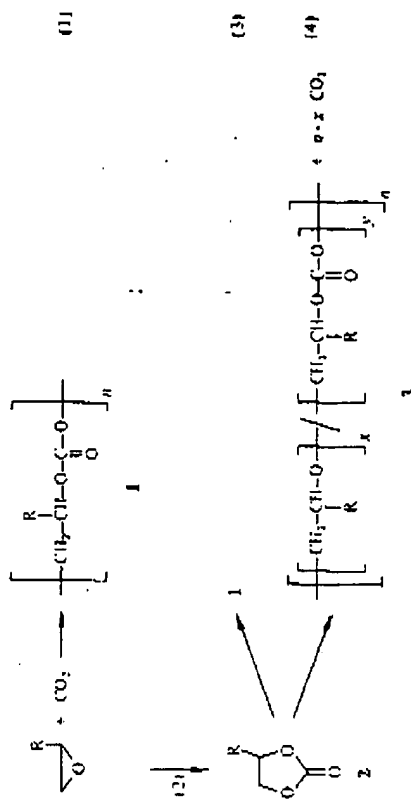
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SUMMARY:

The polymerization of ethylene carbonate using different metal alkoxides results in poly(oxy-ethylene-di-ethylene carbonate). Polymers containing low amounts of CO₂ or pure poly(oxy-ethylene) are formed with anionic and cationic initiators. Poly(ethylene carbonate) is not accessible from ethylene carbonate by variation of temperatures and concentration. The reason is not the low ceiling temperature, but the positive enthalpy of polymerization. A ΔH_p-value of 125.6 kJ/mol was obtained from calorimetric investigations.

Introduction

The use of CO₂ as a synthetic tool in polymer chemistry is reasonable from both an economical and ecological point of view. The direct use of CO₂ was investigated with different comonomers¹⁻³⁾. The copolymerization of oxiranes [Eq. (1)], especially of methyloxirane with CO₂ was investigated most intensively. According to the literature these polymerizations result in a high-molecular-weight aliphatic polycarbonate 1 with a strictly alternating sequence of the monomeric units under proper reaction conditions. A stoichiometric copolymerization is possible with some catalytic systems⁴⁾.



x and y: mole fractions

1	2	3	4
R	H	CH ₃	

5 and 6). The ratio of \bar{M}_n for both experiments is 3, which is equivalent to the reduced amount of ethylene glycol in Exp. no. 6. These telechelic oligomers are not soluble in water and offer a possibility to obtain a hydrophobic prepolymer which can be used e.g. in polyurethane chemistry.

A sequence analysis of 3a showed that ethylene carbonate units are only present in a sequence length one⁶⁾. From these results we can conclude:

At the maximum amount of carbonate units (50%) an alternating copolymer is formed ($x = 1$ and $y = 1$ in 3a).

At amounts of carbonate units lower than 50% a statistical copolymer is formed ($x =$ any integer, $y = 1$ in 3a).

The sequence length one of the carbonate unit may have two reasons from the thermodynamic point of view:

- The reaction temperature is above the ceiling temperature (T_c) of 2a. A requirement to observe T_c is an equilibrium polymerization of 2a which is equivalent to a negative enthalpy of polymerization, ΔH_p .
- The enthalpy of polymerization from 2a to 1a [Eq. (4)] is positive. As the entropy of polymerization, ΔS_p , is negative the free enthalpy of polymerization, ΔG_p , is positive at all temperatures.

If case 1 applies it should be possible to obtain 1a using low temperatures and concentrated solutions. In the second case any influence is impossible from the thermodynamic point of view.

Thus, some polymerization experiments were run at low temperatures. Two types of initiator were used, *sec*-butyllithium (*s*-BuLi) as a typical anionic initiator and methyl triflate as a cationic initiator (Tab. 2). The reaction temperature was varied in the range 100 to -30°C . The polymerization experiments below 40°C were performed in concentrated solutions. 1,2-Dimethoxyethane (DME), 1-methyl-2-pyrrolidone (NMP) and dichloromethane were used as solvents.

Neither with *s*-BuLi nor with methyl triflate polymer 1a is formed. No conversion of the monomer was observed with *sec*-butyllithium (mole ratio 2a/*s*-BuLi = 200; reaction time: 72 h). Poly(oxyethylene) is formed by complete elimination of CO_2 using methyl triflate at temperatures higher than 70°C . These results point out that no

Tab. 2. Results of bulk polymerization of 2a ($1.5 \text{ mol} \cdot \text{l}^{-1}$) for 22 h with methyl triflate (MT) at various temp. Mole ratio 2a/MT = 100

Exp. No.	$T/^\circ\text{C}$	Yield in %	Mol-fraction y in 3a
18	110	98	0
19	100	90	0
20	90	60	0
21	80	28	0
22	70	3	0
24	60 ^{a)}	—	—

^{a)} No conversion takes place below 60°C ; at $T \leq 20^\circ\text{C}$ CH_2Cl_2 was used as solvent.

equilibrium between 2a and 1a [Eq. (4)] is established under these reaction conditions. Investigations below -30°C are not possible, due to the low solubility of 2a. An answer to this problem can only be given by thermodynamic measurements.

Useful information on polymerization reactions can be obtained from considerations of the temperature dependence of the enthalpy ΔH_p and entropy ΔS_p of polymerization. If ΔH_p and ΔS_p in Eq. (7) have the same sign the particularly interesting case arises that the monomer polymerizes only above or below a certain limiting temperature, i.e. an equilibrium polymerization with a ceiling temperature T_c takes place

$$\Delta G_p = \Delta H_p - T \cdot \Delta S_p \quad (7)$$

In order to shed light on the polymerization reactions of 2a we have experimentally determined enthalpies of combustion, $\Delta_c H_f$, and temperature dependences of the heat capacities of the monomer and the polymers separately, employing the accurate method of differential scanning calorimetry.

Product 3a from reaction no. 4, in Tab. 1 was used. 1a (\bar{M}_n (GPC) = 569) was supplied by Bayer Comp. It was synthesized from phosgene and ethylene glycol at low temperatures. The enthalpies of combustion and the heat capacity data are summarized in Tabs. 3 or 4, respectively.

Tab. 3. Enthalpies of combustion ($\Delta_c H_f$) and standard enthalpies of formation ($\Delta_f H_f$)

Substance	$\Delta_c H_f$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_f$ $\text{kJ} \cdot \text{mol}^{-1}$
2	-1161.4	-590.9
3a	-1163.4	-384.3
1a	-1287.0	-465.4
CO_2	—	-393.5 ^{a)}
H_2O	—	-285.9 ^{a)}

^{a)} Literature data¹⁶⁾.

From these data the standard enthalpies of formation, $\Delta_f H_f$ (Tab. 4), and the enthalpies of polymerization (Tab. 5) were calculated, using the usual methods employing Hess' and Kirchhoff's law.

The discussion of Eqs. (3) and (4) on the basis of the thermodynamic relation (7) necessitates the knowledge of the entropy of polymerization, ΔS_p . Owing to the lack of the temperature dependence of the heat capacities of all reaction components for temperatures lower than 180 K the exact determination of ΔS_p and ΔG_p is not possible. Therefore, at present we must resort to a qualitative discussion of trends.

A large positive value is obtained calculating the enthalpy of polymerization of reaction (4). If polymerization should take place the entropy of polymerization, ΔS_p , must increase. This is unreasonable. Three- to seven-membered rings show an entropy

Tab. 4. Heat capacities (C_p) of ethylene carbonate (2a) poly(ethylene carbonate) (1a), poly(oxethylene-*alt*-ethylene carbonate) (3a) and carbon dioxide as function of temperature

T/K	C_p 2a		C_p 1a		C_p 3a		C_p CO ₂ J/(mol · K)
	J/(mol · K)		J/(mol · K)		J/(mol · K)		
180	59,9		88,9		53,9		
190	84,1		81,9		63,9		
200	85,3		81,8		66,7		
210	87,3		83,3		69,5		
220	91,2		85,9		72,1		
230	94,4		89,6		75,1		
240	97,7		92,5		78,6		
250	102,4		98,0		82,0		
260	106,1		104,3		86,3		
265			112,3				
270	110,1		133,8		96,5		
275			159,4		124,9		
280	114,9		153,7		136,4		
290	121,1		155,6		137,8		
298	131,6		157,2		137,9		37,2
300	127,7		157,6		138,0		37,3
306	132,1						
310	149,7		158,7		138,7		37,7
316	198,1						
318	400,6						
320	1214,9		159,4		139,1		38,1
322	1778,4						
324	1708,0						
326	1078,5						
328	682,3						
330	554,6		161,1		139,6		38,5
331,5	515,0						
332,5	596,6						
334	431,4						
336	211,3						
338	167,3						
340	152,3		162,9		141,1		38,9
350	153,2		164,7		143,0		39,3
360	155,4		166,4		144,2		39,7
370	157,6		170,8		144,5		40,1
380	160,3		171,7		145,3		40,4
390	162,0		170,8		147,3		40,8
400	164,2		171,3		147,9		41,2
410	167,3		171,7		148,3		41,5
420	169,5		173,5		147,5		41,8
430	172,6		173,9		143,4		42,3
440	173,0		177,0		145,3		42,6
450	175,2		179,6		146,2		42,9

a) Calculated according to $C_p = a - bT - cT^2 + dT^3$ using the values given by Spencer¹⁹⁾:
 $a = 5,152$, $b = 15,224 \cdot 10^{-1}$, $c = -96,81 \cdot 10^{-5}$ and $d = 2,313 \cdot 10^{-9}$.

Tab. 5. Enthalpies of polymerization of ethylene carbonate forming poly(oxethylene-*alt*-ethylene carbonate) [Eq. (4)] and poly(ethylene carbonate) [Eq. (3)] respectively at different temperatures

T/°C	ΔH_p ^{a)} kJ · mol ⁻¹	ΔH_p ^{b)} kJ · mol ⁻¹
-73	—	124,6
25	2	125,6 ^{b)}
170	-11,7	112,5

a) Cf. Eq. (3).

b) Cf. Eq. (4).

loss by changing the cyclic form to an open chain. Examples are the cyclic ethers²⁰⁾ and lactams²¹⁾. In the present case it can be concluded that the thermodynamically favoured end product is the cyclic monomer and not the linear polymer. This statement is in agreement with the results of the ionic polymerization.

The formation of the alternating polymer [Eq. (4)] has a different thermodynamic basis. From Tab. 5 it is evident that ΔH_p becomes negative at the temperature of 170°C. The reaction is additionally favoured by the fact that the loss of CO₂ compensates for a part of the entropy loss; ΔS_p may even increase. This favours the formation of an alternating product.

The polymerization of propylene carbonate (2b) is analogous to that of 2a. Experiments at low temperature did not result in a conversion using anionic and cationic initiators¹⁵⁾. Poly(oxopropylene-co-propylene carbonate) (3b) can be obtained at 180°C in presence of transesterification catalysts¹⁶⁾. We may deduce that the transformation of 2b into 1b is an endothermic reaction prohibiting as well the formation of 1b.

Experimental part

Reagents: Ethylene carbonate (from Bayer Comp.) was purified as described⁶⁾. Zirconium tetrapropionate (4) (from Fluka) and dibutylmethoxytin (5) (from Merck) were distilled i. vac.

Ethylene glycol (from Hüls) was distilled i. vac. The main fraction was dried with Na₂SO₄ and purified by distillation over a 1,5 m. column, sec-Butyl lithium (from Aldrich, 12% solution in cyclohexane/isopentane) and methyl triflate (MTT) (from Merck) were used as received. *N*-methylpyrrolidone (NMP) was purified by distillation in presence of 4,4'-methylenebisphenyl isocyanate and dibutyltin dilaurate as catalyst. Poly(ethylene carbonate) (1a) (from Bayer Comp.; M_n (GPC) = 569) was prepared from ethylene glycol and phosgene. It was purified by precipitation from acetone/hexane and dried over P₂O₅ at 50°C i. vac.

Dibutylmethoxytin (6): 12,4 g (42,2 mmol) of 5 were added dropwise at room temperature to 10 ml (0,8 mol) of ethylene glycol. The reaction mixture was heated to 100°C and stirred for 2 h. The excess of ethylene glycol was distilled off. The product was dried at 130°C. Yield: 12,1 g (98%).

C ₁₀ H ₂₂ O ₂ Sn (292,97)	Calc.	C 41,00	H 7,56	O 10,92	Sn 40,51
	Found	C 41,32	H 7,75	O 10,61	Sn 40,52

Polymerizations: 88 g (1 mol) of 2a were polymerized with 0.73 g (2.5 mmol) of dibutyltinhydride (DBTH) (6) under nitrogen at 170 °C for 10 days. During this polymerization 17.2 g of CO₂ were separated. 3a was isolated by dissolving in 150 ml of dichloroethane, precipitation into 1.5 l of methanol and drying at 50 °C i. vac. Polymers with molecular weights < 5000 are dissolved in dichloromethane and purified by extraction with 2 M HCl and water. The solution was dried with Na₂SO₄ and the solvent removed i. vac.

Oligomerization of 2a was effected in the same way using the conditions of Tab. I.
Measurements: ¹H NMR spectra were obtained with a Bruker AC-300-Spectrometer in deuteriochloroform. Merckogel OR 1 Mio. and DMF as solvent were used for GPC analyses. A differential calorimeter type DSC 2 of Perkin Elmer was used for DSC measurements.

The DSC measurements were kindly performed at the University of Ulm. Thanks are due to Dr. Höhne for his assistance.

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Intramolecular charge transfer complexes, 28a)

Poly(ω -(*N*-carbazolyl)alkyl methacrylate-co-2-(methacryloyloxy)ethyl 3,5-dinitrobenzoate)s

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SUMMARY:

Copolymers with intramolecular charge transfer interactions were synthesized by radical copolymerization of ω -(*N*-carbazolyl)alkyl methacrylates (where alkyl is propyl and butyl) with 2-(methacryloyloxy)ethyl 3,5-dinitrobenzoate. These copolymers are characterized by a dependence of the electronic absorption, the solubility and the density on the composition. The intramolecular degree of complexation depends on spacer length and exerts a maximum for the spacer with three methylene groups.

Introduction

In a previous paper we reported on the synthesis and polymerization of four novel acrylic and methacrylic monomers containing carbazoyl groups having a spacer between the double bond and the aromatic part, i. e. 3-(*N*-carbazolyl)propyl and 4-(*N*-carbazolyl)butyl acrylate and methacrylate¹⁾. The study of the intermolecular charge transfer complexes (CTC) of the synthesized homopolymers with 2,5-cyclohexadien-1,4-diylidenedimalonitrile (TCNQ) evidences the favourable influence of the spacer having three methylene groups on the complexing capacity of the donor.

Intramolecular CTCs, obtained by the copolymerization of donor and acceptor monomer pairs were studied in the preceding papers of this series^{2,3)}. The intramolecular complexation between electron donor and electron acceptor pendant groups was evidenced by different spectral methods. The copolymers are characterized by the dependence of the colour, electronic absorption, solubility, density and photoconductivity on polymer composition¹⁻⁶⁾.

Following our interest in this field, the present paper reports on the influence of the spacer length of the donor monomer on the intramolecular complexation. Thus, it focuses on the study of the intramolecular CTCs synthesized by radical copolymerization of ω -(*N*-carbazolyl)alkyl methacrylates (alkyl being propyl or butyl) with 2-(methacryloyloxy)ethyl-3,5-dinitrobenzoate. For comparative studies on intramolecular CTC, poly[*N*-(2-carbazolyl)ethyl methacrylate-co-2-(methacryloyloxy)ethyl-3,5-dinitrobenzoate] (1a), whose synthesis was previously reported⁷⁾, was used.

Ring-Opening Polymerization of Ethylene Carbonate and Depolymerization of Poly(ethylene oxide-co-ethylene carbonate)

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ABSTRACT: The ring-opening polymerization of ethylene carbonate (EC) using KOH as initiator was investigated by changing the EC/KOH ratios and the reaction temperatures. The ratio of the rate of polymerization to chain scission increases as the temperature rises. Hydrolysis results and polymer composition data indicate that polymer chains are formed initially by attack of the active polymer chain end (the alcoholate anion) on ethylene carbonate: one attack at the carbonyl group followed by two attacks at the methylene group. Reactions that decrease the molecular weight and carbonate content in the polymer continue as long as the carbonate links are present. A relationship between carbonate content and degree of polymerization was derived using both decarboxylation and bimolecular elimination reactions for the kinetic equations; this fit the experimental data very well.

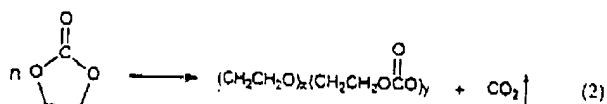
Introduction

Ring-opening polymerization of cyclic monomers depends on both thermodynamic and kinetic factors. Thermodynamically, the free energy change (ΔG_p) should be negative.¹⁻⁵ The free energy change in the polymerization can be determined by the enthalpy and entropy changes (ΔH_p and ΔS_p) and temperature (T):

$$\Delta G_p = \Delta H_p - T\Delta S_p \quad (1)$$

For most cyclic monomers, such as cyclic ethers, lactones, and cyclic siloxanes, ΔH_p and ΔS_p are both negative; they can polymerize only below a certain temperature called the ceiling temperature.¹ Some cyclic monomers, such as cyclooctasulfur and *N,N*-diethylamine-1,3,2-dioxaphosphorinane, with $\Delta H_p > 0$ and $\Delta S_p > 0$, can polymerize only above a certain temperature called the floor temperature.¹ If $\Delta H_p < 0$ and $\Delta S_p > 0$, the monomers can polymerize at any temperature; if $\Delta H_p > 0$ and $\Delta S_p < 0$, polymerization is thermodynamically forbidden.

Five-membered aliphatic cyclic carbonates, such as ethylene carbonate and propylene carbonate, are unique in ring-opening polymerization. Their ceiling temperature is below 25 °C, but they have been polymerized above 100 °C. The repeat units of the resultant polymers were a mixture of monomeric units (carbonate units) and the corresponding oxide units, which means that CO₂ is lost during the polymerization (eq 2). Probably the evolution of the CO₂ makes ΔS_p positive, so this polymerization becomes thermodynamically possible at high temperature.



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Table 1. Five Reaction Conditions Used in This Study

	EC/KOH mole ratio	reaction temp (°C)
case I	1000/1	180
case II	200/1	180
case III	20/1	180
case IV	1000/1	150
case V	1000/1	200

Ethylene carbonate could be polymerized using Lewis acids, transesterification catalysts, or bases as initiators or as polymerization catalysts.⁷⁻¹³ When Lewis acids or transesterification catalysts were used, normally the resultant polymers contained about 40–50 mol % of ethylene carbonate units (reaction temperature was 150–170 °C and reaction time was 70–100 h).^{7-11,13} When base was used, the resultant polymers contained 10–20 mol % of ethylene carbonate links (reaction temperature was about 150 °C and reaction time was 72–98 h).¹² The polymerization mechanism of ethylene carbonate using a basic catalyst has not been reported as far as we know.

In this paper, ethylene carbonate was polymerized with KOH as initiator to study the polymerization mechanism.

Experimental Section

Materials. Ethylene carbonate (EC, from Acros Organics) was dried over P₂O₅ and then fractionally distilled under vacuum.¹⁴ KOH (Fisher Scientific) was dried under vacuum at 110 °C for 3 days using an Abderhalden-type drying apparatus; then it was ground into powder in a porcelain dish under nitrogen or argon atmosphere in a glovebox. The KOH powder was directly used as initiator. The other chemicals were obtained from Fisher Scientific and used without further purification.

Polymerization Procedure. A three-neck 250 mL round-bottomed flask containing a magnetic stirring bar was equipped in a glovebox with a gas inlet/outlet and condenser under nitrogen or argon atmosphere. Then 1.5 mol (132.09 g) of EC and a measured amount of powdered KOH were added to the round-bottomed flask in the glovebox. The mole ratios of EC/KOH used in these systems were 1000/1, 200/1, and 20/1. The

Table 2. 180 °C Reaction Results (EC/KOH mole ratio = 1000/1), Case I

reaction time (h)	convn ^a (%)	carbonate unit content ^b (mol %)	oxide unit content ^c (mol %)	vinyl end group content ^d (mol %)	molecular weight ^e (M_n/M_w)	PDI ^f	M_n and M_w after hydrolysis ^g (M_n/M_w)	$M_{n,hyd}$ ^h	stage
2	26.2	31.8	68.2	0.00	3620/5220	1.45	188/252	132	I
3	39.4	22.7	77.3	0.00	4500/5850	1.30	200/272	184	
5	73.7	19.8	81.2	0.00	5700/7350	1.29	220/310	212	
9	93.5	17.0	83.0	0.00	6900/9040	1.31	240/340	248	
12	98.4	16.9	83.1	0.00	6600/9600	1.45	250/350	249	
15.5	99.9	16.9	83.1	0.00	8400/9860	1.40	260/370	249	II
19	100	17.0	83.0	0.00	5100/7600	1.48	270/380	245	
22	100	15.5	84.5	0.00	2300/3270	1.42	280/430	249	
25	100	14.3	85.7	0.53	1800/2913	1.62	280/430	258	
28	100	13.1	86.9	1.13	1680/2410	1.48	290/430	273	
31.5	100	10.2	89.8	2.04	1250/1860	1.49	310/520	313	
33	100	7.3	92.7	2.00	950/1530	1.61	340/570	359	
35	100	5.9	94.1	2.24	640/1200	1.88		335	
42.5	100	4.0	96.0	2.65	530/943	1.78		347	

^a Determined from eq 3. ^b Determined from eq 4. ^c Determined from eq 5. ^d Determined from eq 11. ^e Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. ^f Polydispersity index = M_w/M_n . ^g Determined from eq 7.

Table 3. 180 °C Reaction Results (EC/KOH mole ratio = 200/1), Case II

reaction time (h)	convn ^a (%)	carbonate unit content ^b (mol %)	oxide unit content ^c (mol %)	vinyl end group content ^d (mol %)	molecular weight ^e (M_n/M_w)	PDI ^f	stage
1	32.6	25.2	74.8	0.00	1880/3420	1.82	I
2	62.1	18.2	81.8	0.00	3700/4920	1.33	
3	91.8	16.5	83.5	0.00	4200/5910	1.41	
4	96.9	15.7	84.3	0.00	4550/6280	1.53	
5	99.1	15.1	84.9	0.00	4050/6960	1.58	
7.5	100	14.1	85.9	0.30	3900/7100	1.82	II
10	100	13.5	86.5	0.67	2610/4950	1.90	
14	100	10.4	89.6	1.87	1680/2660	1.58	
18	100	6.9	93.1	3.27	870/1690	1.94	
24.5	100	0.0	100.0	4.33	530/960	1.81	
31	100	0.0	100.0	4.41	420/770	1.83	
39	100	0.0	100.0	4.45	410/760	1.85	
52	100	0.0	100.0	5.13	420/760	1.81	
62	100	0.0	100.0	4.37	430/770	1.79	

^a Determined from eq 3. ^b Determined from eq 4. ^c Determined from eq 5. ^d Determined from eq 11. ^e Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. ^f Polydispersity index = M_w/M_n .

reaction mixture was stirred at 150, 180, or 200 °C. There were five reaction conditions, shown in Table 1. Ultrahigh purity grade nitrogen or argon gas was continuously passed through the flask during the reaction. About 2 mL of the reaction mixture was sampled at given times using a syringe to prevent air and moisture contamination of the reaction (Tables 2–6). They were directly used for NMR measurements. For GPC measurement, a neutralized sample was used; the reaction mixture was dissolved in THF and neutralized to pH 7 using acetic acid.

Hydrolysis of Polymers. A 0.5 g sample of polymer was added to 5–20 mL of 0.5 N KOH in ethanol. The volume of KOH solution was chosen so that the KOH equivalent exceeded that of the polymer carbonate content. (Determination of the carbonate content will be discussed in the Results and Discussion section.) Normally, a 1.5-fold molar excess of KOH was used. The mixture was stirred at room temperature for 3 h. The reaction mixture was neutralized using 0.1 N HCl aqueous solution and then filtered. Solvent was removed from the filtrate using a rotary evaporator; a viscous liquid was obtained. The viscous liquid was a mixture of poly(ethylene glycol)s; no carbonate groups were left by ¹H NMR. For a reaction mixture that contained monomer (EC), the monomer was removed before the hydrolysis as follows. First, 1.0 g of the reaction mixture was dissolved in 2.0 g of ethanol, and the solution was poured into 100 mL of ether. Viscous polymer

Table 4. 180 °C Reaction Results (EC/KOH mole ratio = 20/1), Case III

reaction time (h)	convn ^a (%)	carbonate unit content ^b (mol %)	oxide unit content ^c (mol %)	vinyl end group content ^d (mol %)	molecular weight ^e (M_n/M_w)	PDI ^f	stage
0.5	69.5	24.6	75.4	0.00	850/1300	1.53	I
1.5	100	13.4	86.6	0.00	1040/1470	1.41	
2.5	100	9.2	90.8	1.32	580/980	1.69	II
3	100	7.3	92.7	1.73	460/740	1.61	
4	100	0.2	99.8	2.58	310/520	1.68	
5	100	0	100	1.69	290/510	1.76	
7	100	0	100	1.94	280/500	1.79	
9	100	0	100	1.88	290/490	1.69	
12	100	0	100	1.99	280/500	1.78	

^a Determined from eq 3. ^b Determined from eq 4. ^c Determined from eq 5. ^d Determined from eq 11. ^e Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. ^f Polydispersity index = M_w/M_n .

precipitated while the monomer (EC) remained dissolved in the ether. The ether layer was then decanted from the reaction. The polymer was washed with ether several times until no monomer was left in the polymer.

Characterization. ¹H NMR (200 MHz) and ¹³C NMR (50 MHz) spectra were obtained using a Varian Gemini 200 spectrometer with CDCl₃ as solvent. Molecular weights were obtained using a Waters model 590 gel permeation chromatography instrument (GPC) equipped with one Phenogel GPC guard column, two Waters Styragel HR 4E columns, and a refractive index detector. THF was used as eluent at a flow rate of 1 mL/min at 40 °C. A calibration plot was constructed using ethylene glycol, tri(ethylene glycol), tetra(ethylene glycol), penta(ethylene glycol), hexa(ethylene glycol), and poly(ethylene glycol) standards (molecular weights ranged from 440 to 13 000).

Results and Discussion

EC (1.5 mol) was bulk polymerized with different amounts of KOH: 0.075, 0.0075, and 0.0015 mol, at 180 °C. Also, 1.5 mol of EC was polymerized with 0.0015 mol of KOH at 150 and 200 °C, Table 1.

The EC/KOH ratio mentioned above might not be exactly correct. Commercial KOH always contains 10–15 wt % of water, and complete removal of the water requires fusion in a vacuum.¹⁵ Three days under vacuum at 110 °C might not have been enough to totally dry the KOH. However, the main concern of this paper is not quantitative analysis but developing a polymeriza-

Table 5. 150 °C Reaction Results (EC/KOH mole ratio = 1000/1), Case IV

reacn time (h)	convn ^a (%)	carbonate unit content ^b (mol %)	oxide unit content ^c (mol %)	vinyl end group content ^d (mol %)	molecular weight ^e (M_w/M_n)	PDI/ stage
1				0.00	990/1050	1.06 I
3	9.0	30.0	70.0	0.00	2000/2300	1.15
5	18.3	25.7	74.3	0.00	4800/5460	1.14
8	28.3	23.1	76.9	0.00	5480/6740	1.23
10	36.8	23.3	76.6	0.00	5700/7500	1.31
13	39.5	23.0	77.0	0.00	5800/7410	1.23
15	43.2	22.6	77.2	0.00	5900/7530	1.28
18	52.1	22.1	77.8	0.00	6960/8130	1.36
24	60.7	21.6	78.4	0.00	5700/7780	1.36
29	68.5	20.9	79.1	0.00	5390/7410	1.37
34	76.6	20.1	79.9	0.00	5070/7390	1.46
37	81.3	19.4	80.6	0.00	5020/7540	1.50
42	86.0	18.7	81.3	0.00	4550/7020	1.54
45	90.5	18.2	81.8	0.00	4410/7000	1.58
51	95.7	18.2	81.8	0.00	4290/6970	1.62
58.5	100	15.9	84.1	0.00	3980/6390	1.61 II
64.5	100	15.5	84.5	0.00	3640/5860	1.61
75	100	15.1	84.9	0.00	3060/5240	1.71
83	100	15.1	84.9	0.01	2310/4860	1.73
94	100	13.1	86.9	0.01	2400/4140	1.73

^a Determined from eq 3. ^b Determined from eq 4. ^c Determined from eq 5. ^d Determined from eq 11. ^e Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. ^f Polydispersity index = M_w/M_n .

Table 6. 200 °C Reaction Result (EC/KOH mole ratio = 1000/1), Case V

reacn time (h)	convn ^a (%)	carbonate unit content ^b (mol %)	oxide unit content ^c (mol %)	vinyl end group content ^d (mol %)	molecular weight ^e (M_w/M_n)	PDI/ stage
1	25.1	28.9	71.1	0.00	5390/6930	1.29 I
2	46.1	20.9	79.1	0.00	7500/10100	1.35
3	73.7	19.0	81.0	0.00	6970/11190	1.25
3.5	85.2	13.9	81.1	0.00	8730/11280	1.29
4	93.4	17.1	82.9	0.00	8420/11410	1.36
4.5	95.8	17.0	83.0	0.00	8270/11260	1.36
5	98.6	16.7	83.3	0.00	8000/10890	1.36
5.5	99.0	16.7	83.3	0.00	7720/10480	1.36
7	99.3	16.0	84.0	0.00	6700/9190	1.37
8	100	16.1	83.9	0.52	5310/8300	1.43 II
9	100	15.8	84.2	0.77	4410/7070	1.60
11.5	100	14.3	85.7	1.13	3100/4210	1.39
14	100	11.9	88.1	1.03	1800/3100	1.72
16	100	10.5	89.5	2.34	1220/2080	1.71
19	100	9.9	90.1	2.88	980/1870	1.91
25	100	5.9	94.1	3.35	760/1530	2.01
32	100	3.5	96.5	4.84	460/1030	2.24

^a Determined from eq 3. ^b Determined from eq 4. ^c Determined from eq 5. ^d Determined from eq 11. ^e Determined from GPC using the calibration curve of standard poly(ethylene glycol)s. ^f Polydispersity index = M_w/M_n .

tion mechanism, so a small amount of possible water impurity will not affect the conclusions. Water in this polymerization acts similarly to KOH in that each molecule generates a polymer molecule.

About 2 mL of the reaction mixture was sampled at a given time to determine conversion, polymer molecular weight, and composition (Tables 2–6). For case I (see Table 1 for conditions), as soon as the system was heated, KOH started to dissolve in the reaction medium, and after about 30 min, all the KOH was dissolved. So the monomer/initiator ratio, 1000/1, is valid after about 30 min. From the beginning of the reaction, gas evolved vigorously from the reaction mixture. Vigorous gas evolution continued for 19 h, and then diminished. No

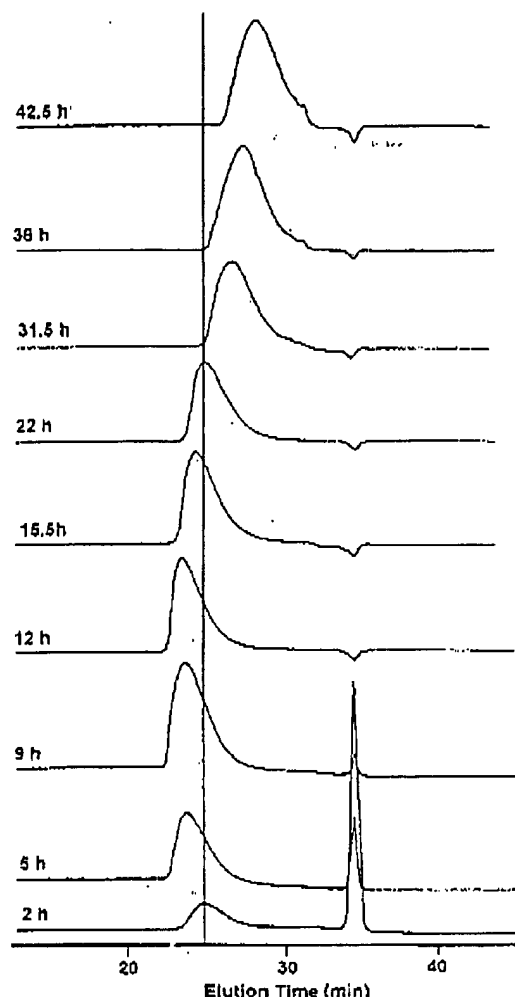


Figure 1. Gel permeation chromatography results for case I (EC/KOH = 1000/1, 180 °C).

gas evolution could be detected after 33 h. The color of the reaction mixture changed during the reaction. Initially the reaction mixture was water white. As soon as the reaction started, the color changed to light yellow (1–12 h), darkened to yellow (12–28 h), to dark yellow (28–38 h), and finally to brown (>38 h). For cases II and III, the KOH powder dissolved completely after 45 min and 2 h, respectively. Gas also evolved vigorously at the beginning of the reaction, and continued until 8 and 2 h for cases II and III, respectively. The colors of the reaction mixtures for these cases changed in the same pattern as for case I, but much faster. For case IV, gas evolution was observed for 94 h, the maximum reaction time. The color of reaction mixture changed very slowly. For case V, little, if any, gas evolved after 11.5 h, and the color of the reaction mixture changed very quickly. A noticeable feature of all the reactions was that the color changed to light yellow as soon as the reaction started.

GPC and NMR spectra were taken for the samples. Figure 1 shows the molecular weight (GPC) change of the reaction mixture with reaction time for case I. The sharp peaks at about 34 min are due to the monomer and the broad peak at earlier elution times is due to the polymer. In the early stage of reaction (1–9 h), both

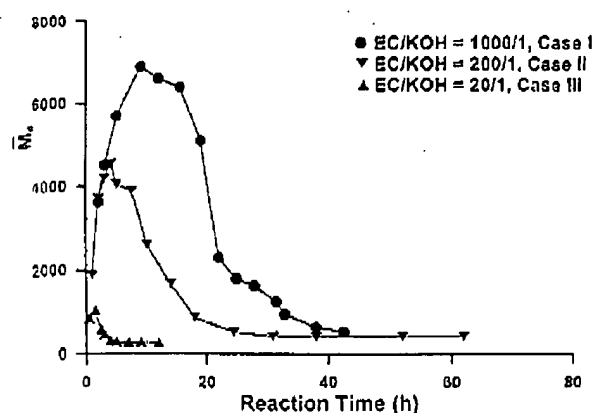


Figure 2. Number-average molecular weight (\bar{M}_n) vs time curves for three 180 °C cases (cases I, II, and III).

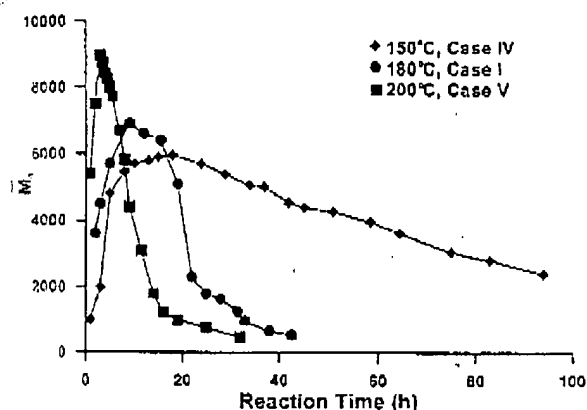


Figure 3. Number-average molecular weight (\bar{M}_n) vs time curves for three EC/KOH = 1000/1 cases (cases I, IV, and V).

monomer and polymer peaks are visible, with the monomer peak intensity decreasing while the intensity of the polymer peak increases. After 12 h, only the polymer peak is visible. The molecular weight of the polymer increases (the elution time decreases) as the reaction time increases up to 12 h and then starts to decrease. GPC number and weight-average molecular weights are listed in Table 2. Molecular weight changes for cases II, III, IV, and V were also observed and are listed in Tables 3–6.

Figure 2 shows the molecular weight change with reaction time for the three 180 °C cases (cases I, II, and III). For every case, molecular weight first increases, reaches a maximum, and then decreases. The times to reach the maximum molecular weight increased as the EC/KOH mole ratios increased; they were about 1.5, 4, and 9 h for EC/KOH = 20/1, 200/1, and 1000/1, respectively. The lower the KOH concentration (the higher the EC/KOH ratio), the higher the maximum \bar{M}_n .

Figure 3 shows the change in \bar{M}_n as a function of reaction time for the three cases where EC/KOH = 1000/1 (cases I, IV, and V). The higher the reaction temperature, the higher the maximum molecular weight of the polymer and the shorter the time to reach the maximum molecular weight. At 180 and 200 °C, the molecular weight decreases rapidly at first after reaching its maximum and subsequently decreases slowly.

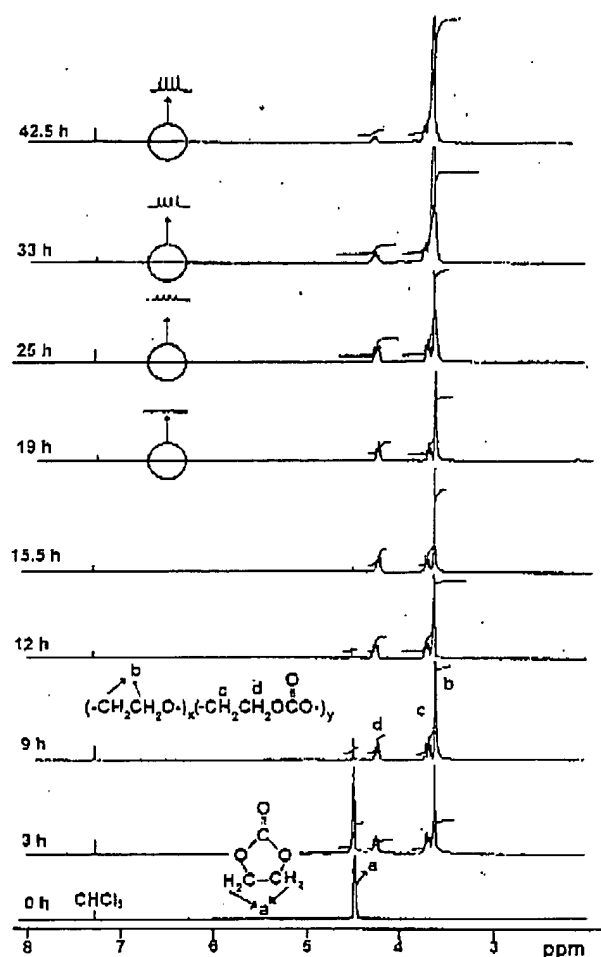


Figure 4. ¹H NMR spectra for case I (EC/KOH = 1000/1, 180 °C).

At 150 °C (case IV), the molecular weight decreases slowly after reaching the maximum.

The maximum \bar{M}_n 's obtained for cases I, II, IV, and V were 6900, 4550, 5960, and 8970. Considering the monomer/initiator ratios, these values are very low. For case III, the maximum \bar{M}_n , 1050, was obtained at 1.5 h. The maximum \bar{M}_n calculated from the monomer/initiator ratio (20/1) and the polymer composition at 1.5 h for case III is 970. In case III, the initiator, KOH, totally dissolved after 2 h. Therefore, the monomer/initiator ratio should be larger than 20/1 at 1.5 h. So in case III, we can also assume that the maximum \bar{M}_n obtained is smaller than that calculated from the monomer/initiator ratio. These results indicate that chain degradation occurred from the beginning of the polymerization. The chain degradation reactions will be explained in the later section of this paper.

The polymer chemical structure was studied by NMR as a function of reaction time and temperature. Figure 4 shows the ¹H NMR spectra of the samples for case I. As the reaction time increased, the peak intensity of the proton due to monomer (EC) (singlet at 4.54 ppm) decreased. After 19 h the polymer structure shows clearly. As expected, it contains ethylene oxide and ethylene carbonate units (eq 2).

By peak integration of these spectra, the monomer conversion and the polymer composition can be calcu-

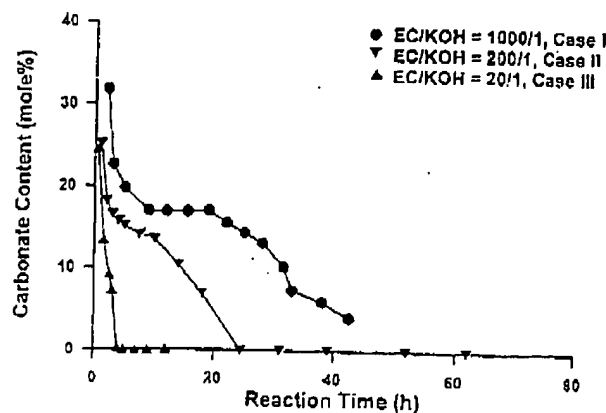


Figure 5. Carbonate content vs time curves for three 180 °C cases (cases I, II, and III).

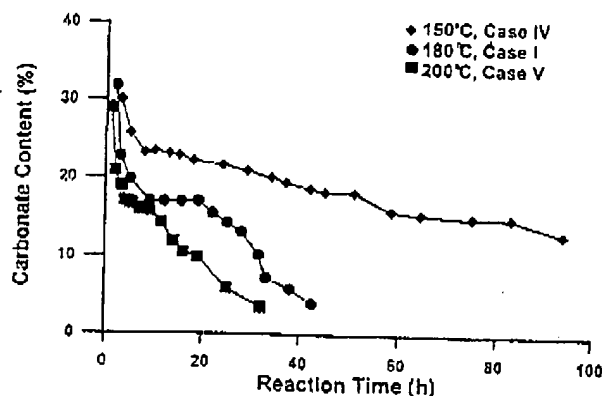


Figure 6. Carbonate content vs time curves for three EC/KOH = 1000/1 cases (cases I, IV, and V).

lated. The degree of conversion was calculated as follows:

$$\text{conversion (\%)} = \frac{A_b + A_c + A_d}{A_a + A_b + A_c + A_d} \times 100 \quad (3)$$

where A_a , A_b , A_c , and A_d are the intensities of the a, b, c, and d protons, respectively (Figure 4). The conversions for all cases were calculated and are listed in Tables 2–6. Figure 5 shows the time vs conversion curves for the three 180 °C cases. The times to reach 100% conversion for EC/KOH = 20/1, 200/1, and 1000/1 cases were 1.5, 7.5, and 19 h, respectively.

The polymer composition was calculated by comparing the area of the multiplet at 3.50–3.66 ppm, assigned to the ethylene oxide (EO) unit, with that of two triplets at 3.70 and 4.26 ppm, assigned to the ethylene carbonate (EC) unit, as follows (Figure 4).

$$\text{EC content (mole \%)} = \frac{A_c + A_d}{A_b + A_c + A_d} \times 100 \quad (4)$$

$$\text{EO content (mol \%)} = 100 - \text{EC content (mol \%)} \quad (5)$$

The composition changes for all the cases were calculated and are listed in Tables 2–6. Interestingly, the EC content is always below 32 mol % even in the earliest stage of the polymerization. Figures 5 and 6 show the changes of the carbonate content in the polymer with

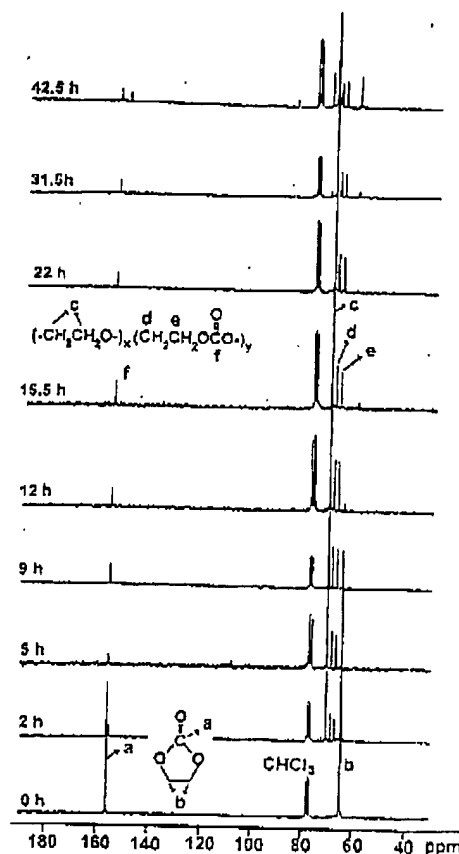


Figure 7. ^{13}C NMR spectra for case I (EC/KOH = 1000/1, 180 °C).

reaction time for all the cases. In general the carbonate content changes in three steps. At first, the carbonate content decreases rapidly from about 30 mol % to about 17–23%. In the second step, it tends to plateau. It decreases steadily to zero in the third step. The structure changes of the reaction mixture and the polymer structure were also confirmed by ^{13}C NMR (Figure 7).

The oxide sequences in the polymer backbone were converted to poly- or oligo(ethylene glycol)s; the carbonate linkage can be easily hydrolyzed^{7,16,17} under basic conditions as follows:

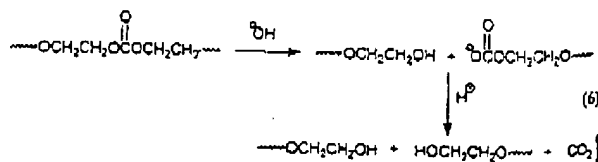


Figure 8 shows the GPC results of the hydrolyzed polymers of case I. In the early stage of the reaction a major peak was observed at 31.8 min elution time. The elution times of ethylene, diethylene, triethylene, and tetraethylene glycols were 32.8, 32.3, 31.8, and 31.4 min, respectively. So, in the early stages a major polymer structure comprises two oxide units and a carbonate unit (EC–EO–EO repeating unit). As the reaction time increased, the average oxide unit length increased (the elution time of the hydrolyzed polymer fragments increased). The M_n 's and M_w 's after hydrolysis for case I are listed in Table 2.

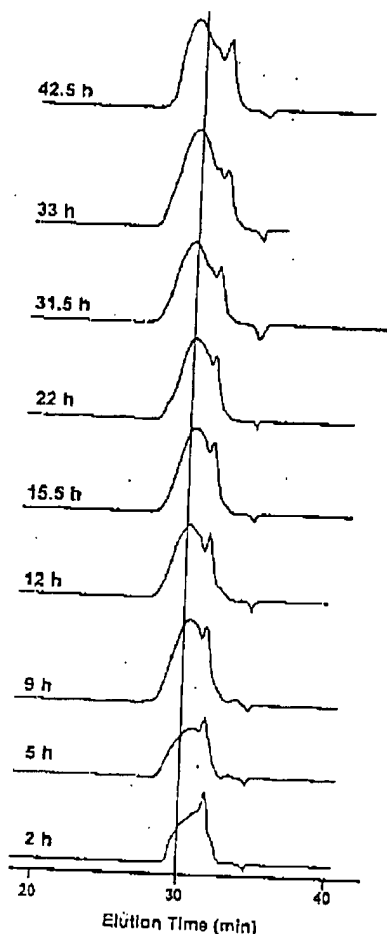


Figure 8. Gel permeation chromatography results after hydrolysis for case I.

\bar{M}_n 's after hydrolysis ($\bar{M}_{n,hyd}$) can also be calculated from the \bar{M}_n 's and oxide/carbonate contents of the polymers as follows:

$$\bar{M}_{n,hyd} = \frac{\bar{X}_n}{(1 + N_{EC})} \times 44.05 \quad (7)$$

Here, \bar{X}_n is the number-average degree of polymerization and N_{EC} is the average number of carbonate units per polymer chain. They can be calculated as follows:

$$N_{EC} = \bar{X}_n \times C_{EC} \quad (8)$$

$$\bar{X}_n = \bar{M}_n / FW_{av} \quad (9)$$

C_{EC} is the carbonate unit mole fraction in the polymer and FW_{av} is the average molecular weight of a backbone unit:

$$FW_{av} = C_{EC} \times 88.06 + C_{EO} \times 44.05 \quad (10)$$

C_{EO} is the oxide unit mole fraction in the polymer, which can be obtained from 1H NMR spectra, and 88.06 and 44.05 are the unit molecular weights of EC and EO, respectively. $\bar{M}_{n,hyd}$'s of case I are listed in Table 2 and

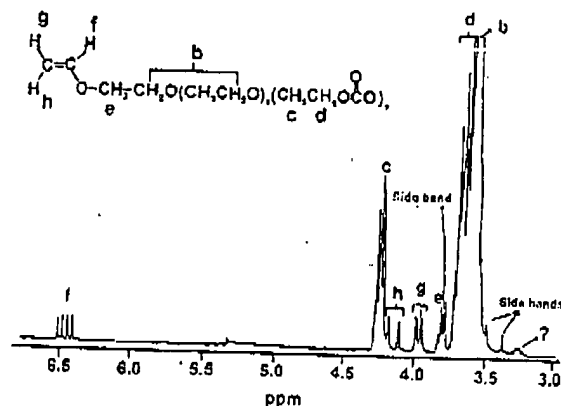


Figure 9. Magnified 1H NMR spectrum for case I after 42.5 h reaction.

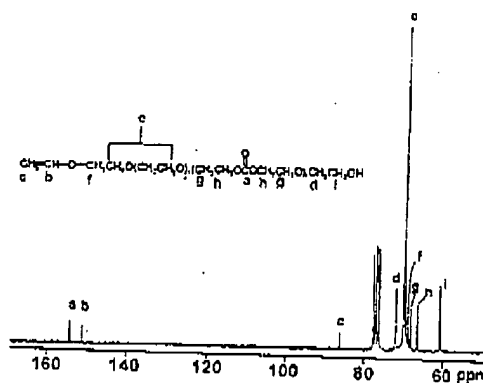
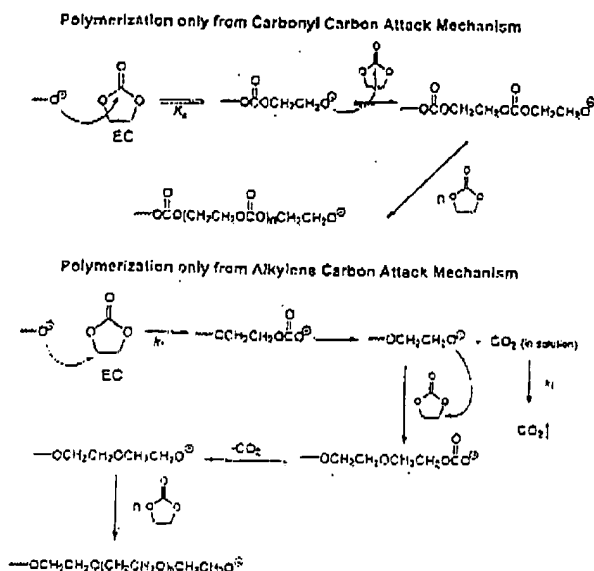


Figure 10. Magnified ^{13}C NMR spectrum for case I after 42.5 h reaction.

they showed quite good agreement with the experimental values.

One interesting feature found in the 1H NMR spectra of the samples is the three deshielded quartets at 3.98, 4.16, and 6.47 ppm and a triplet at 3.82 ppm that started to appear after a certain reaction time. For case I the peaks started to appear after 25 h, as shown in Figure 4. Figure 9 shows peak assignments for the 1H NMR spectrum of case I after 42.5 h reaction. Proton f (chemical shift, $\delta \sim 6.47$ ppm) is strongly affected by the electronegative ether unit and is split by proton h (coupling constant, $J \sim 14.37$ Hz) and by proton g ($J \sim 6.75$ Hz). The proton h ($\delta \sim 4.16$ ppm) signal is split by proton f ($J \sim 14.37$ Hz) and by proton g ($J \sim 2.11$ Hz). The proton g ($\delta \sim 3.98$ ppm) signal is split by proton f ($J \sim 6.75$ Hz) and by proton h ($J \sim 2.11$ Hz). Four peaks are shown in the 3.77–3.86 ppm range. One peak at 3.81 ppm was attributed to a sideband, so the triplet at 3.82 ppm ($J \sim 4.58$ Hz) was attributable to methylene protons (e protons) next to a vinyl ether group. The ^{13}C NMR spectrum (Figure 10) confirms the chemical structure of the case I, 42.5 h reaction. In ^{13}C NMR, a hydroxyethyl end group was also detected (d and i carbon peaks at 72.59 and 61.40 ppm), which was not seen in the 1H NMR spectrum. The vinyl end group molar ratios of the polymers, listed in Tables 2–6, were calculated by comparing the quartet at 6.47 ppm (1H) and the polymer backbone peaks (4H), the multiplet at

Scheme 1



3.50–3.66 ppm, and two triplets at 3.70 and 4.26 ppm as follows.

vinyl end group content (mol %) =

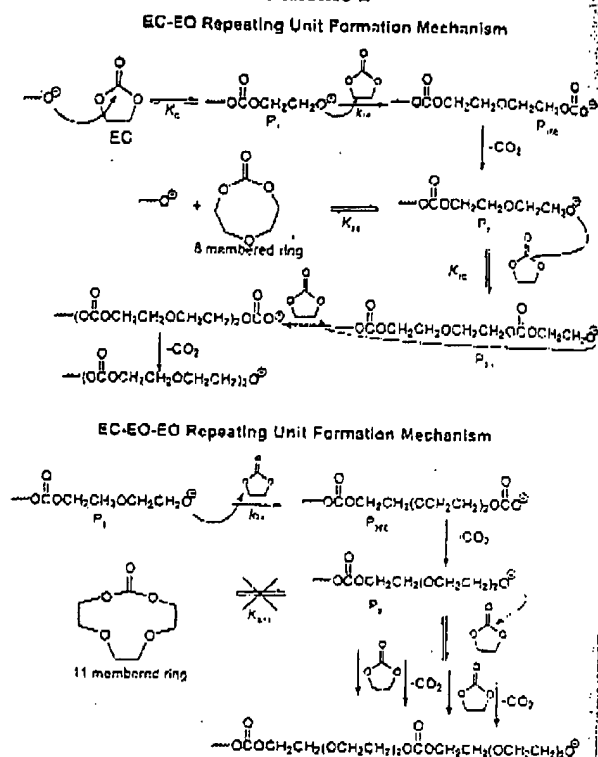
$$\frac{4A_f}{A_b + A_c + A_d + A_e + 4A_f} \quad (11)$$

A_b , A_c , A_d , A_e , and A_f are the intensities of protons b, c, d, e, and f, respectively (Figure 9). The vinyl groups started to appear after the conversion reached 100%, and the concentration increased as the oxide content approached 100 mol %; then they did not change with further heating.

To summarize the above results, the reactions seemed to divide into two stages. During stage I, conversion and molecular weight increase. In stage II, no monomer is left, and the carbonate content and molecular weight of the polymers decrease with time, which indicates that chain cleavage occurs. These stages for all the cases are listed in Tables 2–6.

There are two possible routes to react the monomer during stage I. One is by attack at the carbonyl carbon and the other is by attack at the alkylene carbon (Scheme 1). Kinetically, carbonyl attack is favored over alkylene attack.^{13,17–19} However, the carbonyl attack (K_C) is reversible, and the only way to obtain a high molecular weight poly(ethylene carbonate) is when the polymerization is performed below the ceiling temperature. The polymers obtained in our experiments contained both carbonate and oxide links, the maximum carbonate content found was 32 mol %. Previous papers also mentioned that thermodynamically the cyclic monomer (EC) is favored over the polymer.¹² On the contrary, the attack on the alkylene carbon is irreversible, and is accompanied by decarboxylation. Rokicki et al.²⁰ reported the loss of CO_2 above 150 °C from potassium carbonates, such as 2-(1-phen xy)propyl potassium carbonate. The probable reaction to get polymer from EC is by alkylene attack. However, if the polymerization proceeded only by this reaction, the resulting polymer backbone should be all oxide units. This was not the case.

Scheme 2



Therefore, the most probable EC polymerization mechanism under basic conditions should be a combination of an alkylene carbon attack and a carbonyl carbon attack.

Hydrolysis results show that the EC-EO-EO repeating unit is the major structural unit of the initial polymer. The GPC curves after polymer hydrolysis in the early stage of the reaction (Figure 8, 2 and 5 h) show a diethylene glycol shoulder (32.3 min) on a large single peak from triethylene glycol. This shows that EC-EC repeat unit formation happens, but at much lower frequency than that of EC-EO-EO repeat unit formation. The EC contents at the beginning of the reactions (low conversion) for cases I, IV, and V, 31.8, 30.0, and 28.9 mol %, also confirm this mechanism. For cases II and III, the EC content in the initial polymers was lower, about 25 mol %, probably because decarboxylation was already occurring due to the high base content. The decarboxylation reaction will be examined in a later section.

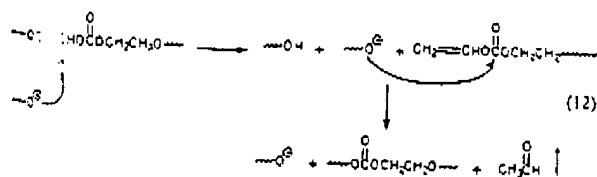
Scheme 2 shows a possible EC polymerization mechanism under basic condition to form the EC-EO-EO repeating unit and the EC-EO repeating unit. In the first step, the active chain end attacks the carbonyl carbon of EC to form P_1 . This equilibrium is to the left side (EC and active end) as mentioned above. Some of P_1 can react with another EC to form P_{1EC} by an attack on the alkylene. This is irreversible. P_2 is then formed by the loss of CO_2 . Then there is another equilibrium, K_{2s} , between P_2 and the eight-membered ring formed by the intramolecular cyclization of P_2 . This equilibrium is reversible and should be toward the P_2 side. If the alcoholate ion end of P_2 attacks the carbonyl carbon of EC (K_{2c}), $P_{2,1}$ will be formed. This reaction is reversible. Then an EC-EO unit can be formed by one alkylene carbon attack, followed by decarboxylation as shown in

Scheme 2, EC-EO Repeating Unit Formation Mechanism. The major reaction of P_2 that leads to chain growth is attack on the alkylene carbon of EC (k_{2A}) to form P_2EC , followed by its decarboxylation to form P_3 . Intramolecular cyclization of P_3 would produce an 11-membered ring ($K_{3,11}$ equilibrium). However, 11-membered ring formation by intramolecular cyclization is rare. It is well-known that five- and six-membered rings form easily by intramolecular cyclization reactions. As the ring size increases from the seven-membered ring, intramolecular cyclization becomes harder, and cyclization is very unlikely if it produces 9- to 12-membered rings. The detailed studies of intracyclization vs linear polymerization can be found elsewhere.^{21,22} We can therefore assume that P_3 is highly favored compared to the 11-membered ring in $K_{3,11}$ equilibrium. By repetition of this mechanism, one carbonyl carbon attack (K_C) and two alkylene carbon attacks (k_{1A} and k_{2A}), polymers with EC-EO-EO repeating units can be formed.

The polymerization mechanisms described above were hypothesized using the assumption that the active center is the alcoholate anion, even though the carbonate anion preferentially exists in the reaction mixture. The alcoholate anion is a much stronger nucleophile than the carbonate anion. For all-base polymerization of lactones, except for the strained β -propiolactone, the alcoholate anion was the active center.^{1,19,23-26} It is reasonable therefore to expect that the active center for the nonstrained EC polymerization is the alcoholate anion.

In stage I, carbonate content decreases. If the CO_2 is lost only during the polymerization step, the polymer oxide content should not change. If the EC is polymerized following the EC-EO-EO repeat unit formation mechanism, shown in Scheme 2, the carbonate content should always be about 33 mol %. For case 1, at the beginning of the reaction, the EC content was 31.8 mol %, while at the end of stage 1 the EC content was down to 18.8 mol %. The difference between the two should be due to the loss of the carbonate group in the polymer chain. There are two possible decarboxylation mechanisms, one is intramolecular while the other is intermolecular, as shown in Scheme 3.

During the polymerization, water white liquid distilled from the reaction mixture and was collected. ^1H NMR analysis showed that the liquid was acetaldehyde. The probable route for the formation of the acetaldehyde is shown in eq 12. When acetaldehyde is formed, it

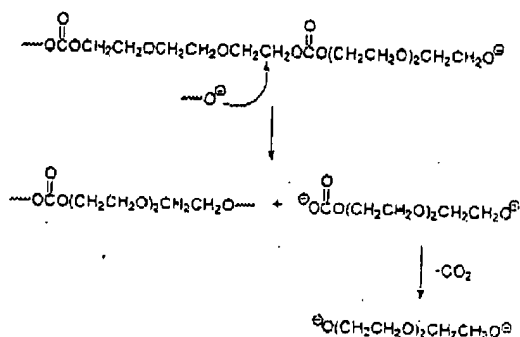
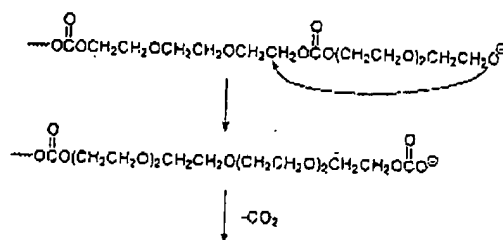


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Scheme 3

Decarboxylation from the Carbonate Group in the Polymer Chain

1. Intramolecular decarboxylation



and darkened as the reaction proceeded. There might be other side reactions which decrease the molecular weight, such as radical chain reactions, observed during the thermal degradation of polyethers and poly(ethylene terephthalate).^{27,28} However these reactions occur at higher temperatures; there is no evidence for them in the present study.

In stage II, all the EC has reacted. In this stage, carbonate content and molecular weight decrease with time, which indicates that polymer chain is cleaved, with CO₂ loss. The decarboxylation reaction, shown in Scheme 3, rationalizes the decrease of carbonate content, but cannot explain the chain cleavage. In stage II, vinyl end groups begin to form, which must be related to the chain cleavage. The vinyl end group can be formed by two possible elimination mechanisms (Scheme 4). One is pyrolytic elimination (Ei) and the other is bimolecular elimination (E2).²⁸ Ei does not seem to happen. Because Ei is a first-order reaction, it can happen as soon as carbonate groups are incorporated into the polymer backbone. However, vinyl groups only started to form in stage II.

$$-d[\text{Car}]/dt = k_{E2}[\text{RO}^-][\text{Car}] + k_{d_{\text{Car}}}[\text{RO}^-][\text{Car}] \quad (13)$$

[Car] is the concentration of carbonate groups in the polymer, and k_{E2} and k_{decar} are the rate constants for the E2 reaction and decarboxylation. In eq 13, k_{E2} is

Scheme 4

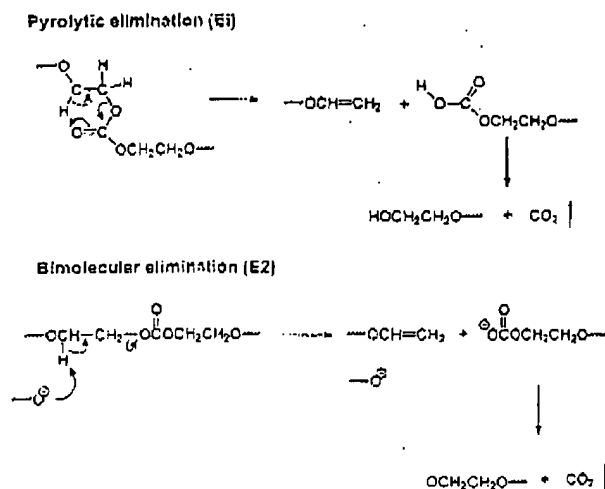


Table 7. Data for Equation 17

reacn time (h)	[Car] ^a (fraction)	FW _{av} ^b	M _n	X _t ^c	case
19	0.170 ^d	51.48	5100	99.07 ^e	I
22	0.155	50.82	2300	45.26	
25	0.143	50.29	1800	35.79	
28	0.131	49.76	1630	32.75	
31.5	0.102	48.48	1250	25.78	
33	0.073	47.21	950	20.12	
38	0.059	46.59	643	13.80	II
42.5	0.040	45.76	527	11.52	
7.5	0.141 ^d	50.20	3900	77.68 ^e	
10	0.135	49.94	2610	52.26	
14	0.104	48.58	1680	34.58	
18	0.069	47.04	870	18.50	
24.5	0	44.05	530	12.05	III
1.5	0.134 ^d	49.90	1040	20.84 ^e	
2.5	0.092	48.05	530	12.07	
3	0.073	47.21	460	9.74	
4	0.002	44.09	310	7.03	
58.5	0.159 ^d	51.00	3980	78.05 ^e	IV
64.5	0.155	50.82	3640	71.63	
75	0.151	50.64	3060	60.42	
83	0.151	50.64	2810	55.49	
94	0.131	49.76	2400	48.23	
8	0.160 ^d	51.08	5310	113.73 ^e	V
9	0.158	50.95	4410	86.55	
11.5	0.143	50.29	3100	61.64	
14	0.119	49.24	1800	36.56	
16	0.105	48.62	1220	25.09	
19	0.099	48.36	930	20.27	
25	0.069	46.60	760	16.31	
32	0.035	45.54	460	10.10	

^a Carbonate content in the polymer. ^b Average molecular weight of backbone unit in the polymer, calculated from eq 10. ^c Average number of backbone units in the polymer. ^d Initial carbonate content, [Car]₀, in stage II. ^e Initial average number of backbone units in the polymer, X₀ in stage II.

Upon integrating eq 15, we obtain eq 16. Cleavage

$$[\text{Car}]_{\text{E2},t} - [\text{Car}]_{\text{E2},0} = \frac{k_{\text{E2}}}{k_{\text{E2}} + k_{\text{decar}}} ([\text{Car}]_0 - [\text{Car}]_t) \quad (16)$$

occurs only during an E2 reaction. If carbonate mole fraction in the polymer is used for the units of [Car] and [Car]_{E2}, [Car]_{E2,t} - [Car]_{E2,0} can be rewritten as $1/\bar{X}_t - 1/\bar{X}_0$, where \bar{X}_t and \bar{X}_0 are the degrees of polymerization at a given time and at the beginning. Therefore, the relationship of carbonate content vs degree of polymerization is given by eq 17. Good straight-line plots.

$$(1/\bar{X}_t - 1/\bar{X}_0) = \frac{k_{\text{E2}}}{k_{\text{E2}} + k_{\text{decar}}} ([\text{Car}]_0 - [\text{Car}]_t) \quad (17)$$

Figure 11, show that this equation gives a good representation of our data (Table 7). From the slope of the line, we can get the ratio between the elimination (k_{E2}) and the unimolecular decarboxylation (k_{decar}) rates, which is shown in Figure 11. The slopes of cases I and II (relatively small amount of initiator) are identical within experimental error, while that of case III (relatively large amount of initiator) is larger than those of cases I and II. As the reaction temperature increases for the three EC/KOH = 1000/1 cases (cases I, IV, and V), the slope increases, indicating that raising the temperature raises the elimination rate relative to the bimolecular cleavage rate. The bimolecular elimination rate constant was found to obey the Arrhenius relation.

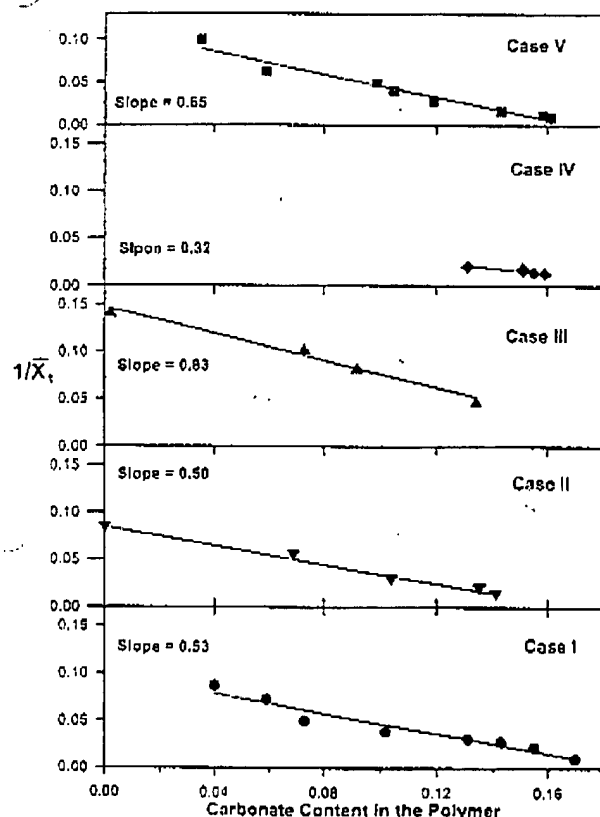


Figure 11. $1/\bar{X}_t$ vs carbonate content curves. The solid line is a fit using eq 17. The slope is $k_{\text{E2}}/(K_{\text{E2}} + K_{\text{decar}})$.

related only to chain cleavage. This is shown in eq 14,

$$d[\text{Car}]_{\text{E2}}/dt = k_{\text{E2}}[\text{RO}^-][\text{Car}] \quad (14)$$

where [Car]_{E2} is the concentration of carbonate groups in the polymer chain that will be cleaved by the E₂ reaction. Then, dividing eq 14 by eq 13, we can eliminate the [RO⁻] term.

$$d[\text{Car}]_{\text{E2}} = -[k_{\text{E2}}/(k_{\text{E2}} + k_{\text{decar}})] d[\text{Car}] \quad (15)$$

ship, $k_{E2}/(k_{E2} + k_{decar}) = A \exp(-E^*/RT)$ ($r^2 = 0.991$), and the apparent activation energy is ~ 23.9 kJ/mol.

Conclusions

Our studies show that $-OCO_2CH_2CH_2OCH_2CH_2OCH_2CH_2-$ (EO-EO-EO) is the major backbone repeat in the early stage of the ring-opening polymerization of ethylene carbonate in basic condition. These repeats can be formed by the combination of two alkylene carbon attacks and one carbonyl carbon attack by the active chain end, as shown in Scheme 2. However the carbonate content in the polymer decreased throughout the polymerization by intermolecular and intramolecular decarboxylation reactions (Scheme 3). Once all the monomer was consumed, bimolecular elimination (E2, Scheme 4) was postulated to happen. The E2 elimination reaction generates vinyl end groups.

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COPOLYMERIZATION REACTIONS OF CARBON DIOXIDE

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KEYWORDS: copolymerization, sequestration, carbon dioxide**ABSTRACT**

Polymerization reactions of carbon dioxide were investigated with a view toward utilization of vast amounts as a chemical feedstock. Copolymerization of carbon dioxide with formaldehyde and paraformaldehyde in the presence of a variety of catalysts was investigated. In the presence of amine catalysts or Lewis acid catalysts, carbon dioxide copolymerizes with formaldehyde or paraformaldehyde to give a water-soluble polymer of polycarbonate structure. A 1:1 alternating copolymer is proposed from its infrared spectra showing a strong ester band at 1750 cm^{-1} . From high-pressure liquid chromatography analysis, number-averaged molecular weight was determined to be about 20,000. However, mixing in 25% of a comonomer spacer (ethylene glycol) gave a polymer with twice the molecular weight. The addition of boric acid resulted in cross-linking of the polymer and a significant increase in the viscosity of the aqueous solution.

INTRODUCTION

Since 1969 when Inoue and coworkers (1, 2) first reported the synthesis of high-molecular-weight poly(propylene carbonate) by copolymerization of CO_2 and propylene oxide using organozinc catalysts, copolymerization of carbon dioxide has been widely studied (3). Because of the low cost and availability of the monomers and the attractive properties of polycarbonates, there has been considerable recent interest in the development of catalysts for the alternating copolymerization of carbon dioxide with epoxides (3-7). Recently, Chiang (8) reported copolymerization of carbon dioxide and formaldehyde to give a 1:1 alternating copolymer. The nature of the product from alternating copolymerization of CO_2 with carbonyl compounds in the presence of a variety of acid and base catalysts is reported here.

EXPERIMENTAL

Reactions were conducted in a 300-mL pressurized Parr autoclave with generally 16 g of CO_2 and an equimolar amount of aldehyde equivalent with 3% by weight of catalyst. Products were worked up differently depending on the solvent for the reaction. In a typical run, a mixture of aqueous formaldehyde (37%), catalyst, and dry ice was placed in a 300-mL Parr reactor. The reactor was sealed under nitrogen and heated at the desired temperature for the desired time period. The reaction products were soluble in the water solvent used for the reaction. For the reactions of paraformaldehyde and trioxane, methyl tertiary butyl ether (MTBE) or dioxane were used as solvents.

Polymer products were analyzed by infrared (IR) spectroscopy and gel permeation chromatography (GPC). Aqueous solutions of the polymeric products were analyzed with high-pressure GPC on a TSK30 gel column with water eluent and ultraviolet (UV) detection at 210 nm, and dioxane solutions were analyzed with a mixed pore size photoluminescence gel column in tetrahydrofuran (THF) solvent. Molecular weights (M_n) were calibrated using retention times of proteins and polymer standards with narrow M_n distributions. Reaction yields were also determined on the GPC column. The copolymer peak area was calibrated using a known concentration of a standard consisting of a purified copolycarbonate sample.

RESULTS AND DISCUSSION**Base Catalysts**

A comparison of the catalytic effects of a series of organic bases was conducted on the reactions of carbon dioxide with aqueous formaldehyde to form the acetal copolycarbonate ester (Figure 1). The reactions were performed in a pressurized autoclave at 120°C using organic bases, methylamine (TEA), dimethylaminopyridine (DMAP), and diazabicyclooctane (DABCO) as catalysts for the reactions (Table I). Chiang used TEA as the catalyst (8). The DMAP and DABCO are much more basic and were expected to exert a better catalytic effect.

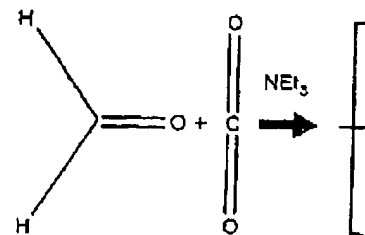


Figure 1. Acetal copolycarbonates

TABLE I

Aldehyde	Catalyst	Reactions of Formalde		
		Solvent	Temp., $^\circ\text{C}$	Time, hr
HCHO (37%, 40 mL)	TEA (2 g)	Water	120	100
HCHO (37%, 40 mL)	DMAP (2.3 g)	Water	120	100
HCHO (37%, 40 mL)	DABCO (2.24 g)	Water	120	100

* HCHO = formaldehyde.

The product from aqueous formaldehyde reaction was with ether recovered about 70% of the base catalyst. The determined by GPC. Polymer peaks eluted early, and determined from retention times and peak areas. Low-mole in the products, as evidenced by the presence of a late GPC higher yields of polymer were obtained from the reaction us gave the lowest yield and is the most volatile.

Water was removed from the reaction products & reaction products were tacky solids with good water and THF and dioxane. IR spectroscopy of the products indicates ester carbonyl groups were present, verifying that the de polycarbonate ester had occurred.

A comparison of the reaction conditions was also formaldehyde using the base catalyst, DMAP. This reac 200°C and the reaction time (12 versus 24 hr). Relevant series of runs, polycarbonate yields increased with temper 175°C , 9%; 200°C , 11%. Increasing the reaction time in 2-5% to 7%. The molecular weight of the polymer products reactions, but was 40,000 for the reaction at 175°C .

Two disadvantages of the aqueous formaldehyde for 1) the product polymers are not easily separated from th owing to similarity in solubility and difficulty in di decomposition; 2) the aqueous formaldehyde contains a commercial formalin solution) that could cap the ends of and formal acid are also formed as byproducts in the aldehydes in base. Although it is displacable from the en reaction and prevent the reaction with the CO_2 .

Copolymerization of Carbon Dioxide and Epoxide with Organometallic Compounds

By SHOHEI INOUE, HIROKUNI KONUMA, and TEIJI TSUBOTA

(Eingegangen am 4. Juli 1969)

SUMMARY:

Attempts to copolymerize carbon dioxide with epoxide led us to the first success in using carbon dioxide as a direct starting material for synthesizing high polymers. Some organometallic catalyst systems were found to catalyze the alternate copolymerization of carbon dioxide and epoxide, resulting in the formation of polycarbonates, the structures of which were confirmed with the aid of IR, NMR and elemental analysis. Diethylzinc-water system produces methanol insoluble aliphatic polycarbonate of much higher molecular weight than that produced by polycondensation. Thermal properties of the methanol insoluble polycarbonate were studied by differential thermal analysis and thermogravimetric analysis.

ZUSAMMENFASSUNG:

Versuche, Kohlendioxid mit Epoxiden zu copolymerisieren, führten zu einem ersten Erfolg bei dem Gebrauch von CO₂ als einem direkten Ausgangsprodukt zur Synthese von Hochpolymeren. Es wurden einige metallorganische Katalysatorsysteme gefunden, die die alternierende Copolymerisation von CO₂ und Epoxid katalysieren, wobei sich Polycarbonate bilden, deren Struktur mit Hilfe der IR-, der NMR- und der Elementaranalyse gesichert wurde.

Durch ein Diäthylzink-Wasser-System entstanden in Methanol unlösliche aliphatische Polycarbonate von wesentlich höherem Molekulargewicht als bei den durch Polykondensation entstandenen Polycarbonaten. Die thermischen Eigenschaften der in Methanol unlöslichen Polycarbonate wurden durch die Differentialthermoanalyse und durch die thermogravimetrische Analyse untersucht.

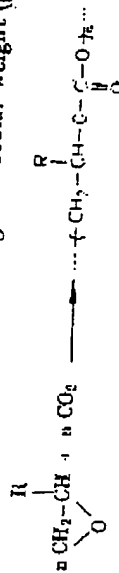
Introduction

Although extensive work has been carried out on the polymerization of carbon-carbon double bond compounds by organometallic compounds, studies on the polymerization, and especially on copolymerization of hetero multiple-bond compounds were still rather undeveloped. Recently some hetero multiple-bond compounds such as isocyanate^{1,2}, carbon monoxide³, and sulfur dioxide⁴ were reported to form copolymers with epoxide, but their molecular weights were still rather low.

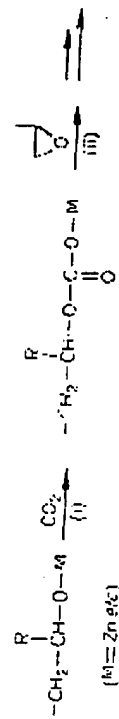
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Copolymerization of Carbon Dioxide and Epoxide with Organometallic Compounds

Carbon dioxide, one of the simplest hetero multiple-bond compounds, is considered to be fairly inactive and has not been regarded as a monomer for synthesizing high polymer. The first success⁵ in using carbon dioxide as a direct starting material for synthesizing high polymer was achieved by us in the alternate copolymerization with epoxide by organometallic compound as catalyst. Our previous communication reported the formation of aliphatic polycarbonate of high molecular weight ($[\eta] > 1$).



Low molecular weight polycarbonates were known to be formed with metal halide or metal carbonate^{6,7}. Usual methods for preparing polycarbonate are polycondensation between bisphenol and phosgene or between bisphenol and diethyl carbonate. In fact, polycarbonate composed of bisphenol A and phosgene is produced industrially as one of the useful resins which has excellent properties with respect to heat and to shock. But aliphatic diols do provide only low molecular weight polycarbonates by these methods^{8,9}. Therefore, our method comprises a novel and useful route towards aliphatic polycarbonates of high molecular weight, since, in some cases, the copolymerization between carbon dioxide and an epoxide was found to proceed substantially alternate. Among the catalysts examined diethylzinc-water system was the most effective for the copolymerization. The catalyst activity of diethylzinc was expected when we started to try copolymerization between carbon dioxide and epoxide, since the successive occurrence of two elementary reactions for alternate copolymerization, (i) and (ii) as shown below, was anticipated from our former studies on the copolymerization of epoxide with acid anhy-



drides^{10,11} or with α -amino acid N-carboxy anhydrides¹² using diethylzinc as catalyst. In fact, the diethylzinc-water system was found to be efficient for the copolymerization of carbon dioxide (CO₂) and propylene oxide

¹³ In relation to this work, HAMANN *et al.*¹⁴ proposed an anionic mechanism for the copolymerization of acid anhydride with cyclic ether by various salts and bases, such as LiCl, KOH, and tetraethylammonium chloride.

insoluble polymer is found to be substantially poly-propylene carbonate, i.e. an alternate copolymer of CO₂ and PO. It is a white solid, soluble in benzene, tetrahydrofuran, acetone, and methylene chloride, but insoluble in methanol, petroleum ether, and cyclohexane. Its molecular weight is considerably high since its intrinsic viscosity measured in benzene at 30°C is sometimes larger than 1.0. Comparison between No. 44 and No. 48 in Table 1 shows the temperature dependency of the copolymerization using the ZnEt₂/H₂O system: the higher temperature brought about the higher yield and the lower molecular weight of the copolymer; in addition the content of carbonate units estimated in the IR spectra is less. The formation of propylene carbonate, which is the cyclic monomer, was also detected by vapor phase chromatography on the reaction mixture, but in very small amount, for experiments carried out at room temperature. However, the possibility that copolymerization would proceed via the intermediate of propylene carbonate could be excluded by the failure of polymerizing propylene carbonate itself under similar conditions.

Products obtained in low yield using calcium-zinc-tetraethyl and *n*-butyllithium as initiators (No. 30 and 31) also contain some carbonate units, as established from their IR spectra. On the other hand, triethylaluminum systems as initiators yield products in rather higher yield than with ZnEt₂/H₂O, which are almost soluble in methanol or in petroleum ether with little turbidity (cf. No. 26 and 27). From IR spectra they were shown to be poly-PO, with very few carbonate units.

From a preparative point of view the ZnEt₂/H₂O system is the most effective among the catalysts examined, so we will discuss this system in some detail in later sections (1.3 and 1.4).

1.2. Structure of PO/CO₂ copolymer

Table 2, Fig. 1, and Fig. 2 present, respectively, elemental analysis data, IR spectrum, and NMR spectrum of methanol insoluble portion of a PO/CO₂ copolymer obtained with ZnEt₂/H₂O system at room temperature (No. 38).

Table 2 Elemental analysis of PO/CO₂ copolymer (Methanol insoluble portion of No. 38)

Element	Obsd. value (%)	Calcd. value (%)	...
C	47.38	47.06	... [-CH ₂ -CH(CH ₃)-O-CO-O] ...
H	5.98	5.92	
O	46.64	47.02	
		62.04	
		10.41	
		27.55	

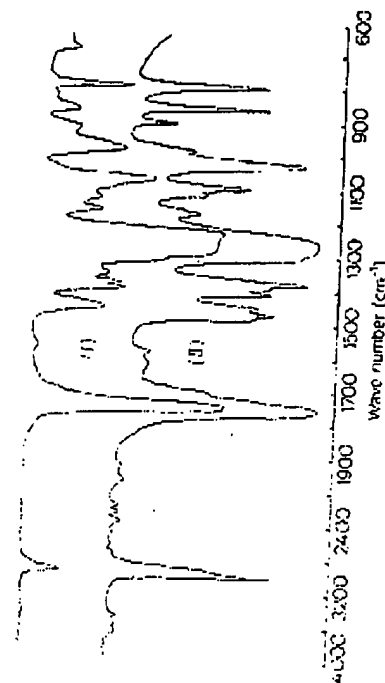
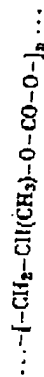


Fig. 1. IR spectra of PO/CO₂ copolymer. (I) MeOH insoluble portion of No. 38. (II) Diethyl carbonate

Table 2 shows that the observed elemental analysis data coincide with the calculated value for polypropylene carbonate



The IR spectrum shows strong absorptions around 1745 and 1250 cm⁻¹ (Fig. 1). By comparison with the spectrum of diethyl carbonate these absorption bands can be assigned to carbonate groups formed by reaction between PO and CO₂. NMR spectrum in Fig. 2 may be assigned as shown in Table 3. The peak expected from poly-PO unit around $\tau = 6.5$ could not be observed.

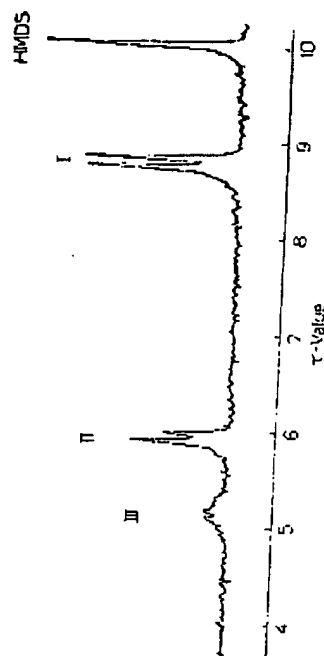


Fig. 2. NMR spectrum of PO/CO₂ copolymer (MeOH insoluble portion of No. 38). Solvent: CDCl₃. Conc.: 4 wt.-%. Temp.: 60°C. Standard: Hexamethyldisiloxane (HMDS)

All these results confirm the formation of an almost completely alternate copolymer from PO and CO₂.

Table 3. Assignment of NMR spectrum in Fig. 2

	τ -Value	Area ratio	Assignment
I	8.8	3.1	...-[-CH ₂ -CH(CH ₃)-O-CO-O-] _n ...
II	5.9	1.9	...-[-CH ₂ -CH(CH ₃)-O-CO-O-] _n ...
III	5.1	1.0	...-[-CH ₂ -CH(CH ₃)-O-CO-O-] _n ...

1.3. Effect of the composition of ZnEt₂/H₂O system on the catalyst activity

As already described, the ZnEt₂/H₂O system is effective for the copolymerization of PO/CO₂. ZnEt₂ itself, however, seems to be almost inactive as shown in Table 1. These facts suggest the important role of molar ratio of ZnEt₂ to H₂O in the copolymerization, as it is for the polymerization of epoxide by the same catalyst system. To confirm it we examined the dependency of the copolymer yield upon molar ratios of H₂O/ZnEt₂ system.

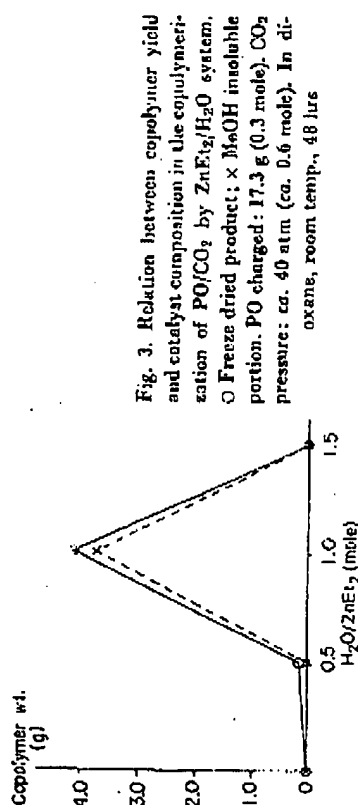


Fig. 3. Relation between copolymer yield and catalyst composition in the copolymerization of PO/CO₂ by ZnEt₂/H₂O system. O Freeze dried product; x MeOH insoluble portion. PO charged: 17.3 g (0.3 mole). CO₂ pressure: ca. 40 atm (ca. 0.6 mole). In dioxane, room temp., 48 hrs.

The results presented in Fig. 3 show the polymer yield to be highly dependent on the H₂O/ZnEt₂ ratio with a clear optimum point at 1:1; this fact may help determining the copolymerization mechanism, since active species of the H₂O/ZnEt₂ system are known to change remarkably according to H₂O/ZnEt₂ ratio, as reported by TSURUTA and TSUCHIYA¹⁰. H₂O/ZnEt₂ system has a cationic character with molar ratios less than 1 and a coordinate anionic nature with molar ratio around 1.0.

1.4. Relative reactivity of PO and CO₂ toward ZnEt₂/H₂O system

Copolymerization of CO₂ with PO by ZnEt₂/H₂O (1:0.9) at various pressures of CO₂ gave the results shown in Table 4. Methanol insoluble polycarbonate was formed even in the presence of an excess of PO, con-

Table 4. Relative reactivity of PO and CO₂ in the copolymerization by ZnEt₂/H₂O system^{a)}

No.	PO		CO ₂		Polymer	
	(g)	(mole)	(atm)	(mole) ^{b)}	Freeze dried (g)	MeOH insoluble (wt.-%) ^{c)} C.U. (%) ^{d)}
39	7.0	0.12	27	ca. 0.40	0.54	91
42	13.9	0.24	20	0.29	0.51	78
41	10.6	0.32	16	0.24	0.52	75
40	27.9	0.48	9	0.12	0.49	62

^{a)} In dioxane, room temp., 48 hrs.

^{b)} Total.

^{c)} Carbonate unit determined from elemental analysis value.

firming the alternate nature of the copolymerization. Since higher pressure of CO₂ resulted in the increase of the methanol-insoluble portion and of the carbonate units, the composition of copolymer can be controlled by changing the pressure of CO₂.

2. Copolymerization of carbon dioxide with epoxide other than PO

We expected to extend this type of copolymerization to form aliphatic polycarbonate of high molecular weight, by examining the possibility of copolymerization with other epoxides than PO.

2.1. Copolymerization with ethylene oxide, styrene oxide, epichlorohydrin, and isobutylene oxide.

Results of the copolymerizations of CO₂ with the above epoxides by ZnEt₂/H₂O system are summarized in Table 5. As in the case of PO, ethylene oxide (EO), styrene oxide (STO), epichlorohydrin (ECH), and isobutylene oxide (IBO) were found to form polycarbonates which are

Table 5. Copolymerization of CO₂ with several epoxides

No.	Epoxide		CO ₂ pressure (atm)	Solvent	Time (hrs)	Polymer formed	
	(g)	(mole)				Freeze dried (g)	MeOH insol. (g)
19	ECH	18.5	0.2	benzene	56	0.83	n.d.
22	STO	24.0	0.2	benzene	24	n.d.	0.51
43	EO	14.2	0.3	dioxane	113	2.79	1.10 ^{a)}
54	IBO	4.3	0.06	dioxane	240	0.20	0.06

Catalyst: ZnEt₂/H₂O (1:0.9) 4 mole-% for epoxide. Temp.: Room temp. (ca. 20°C).

ECH: Epichlorohydrin; STO: Styrene oxide; EO: Ethylene oxide; IBO: Isobutylene oxide

^{a)} $[\eta] = 0.98$ (in chloroform at 30°C).

soluble in methylene chloride and can be purified by reprecipitating from methylene chloride solution with methanol. Copolymer of EO/CO₂ is a white solid with little elasticity like that of PO/CO₂, but its solubility is decreased, since it turned to be insoluble in benzene and acetone. Copolymers of ECH/CO₂ and STO/CO₂ are white powder.

2.2. Structures of the copolymers

It is easy to persuade us to believe the formation of polycarbonate, since the IR spectra of these copolymers (Fig. 4) are quite different from those of polyethers obtained by homopolymerisation of these epoxides;

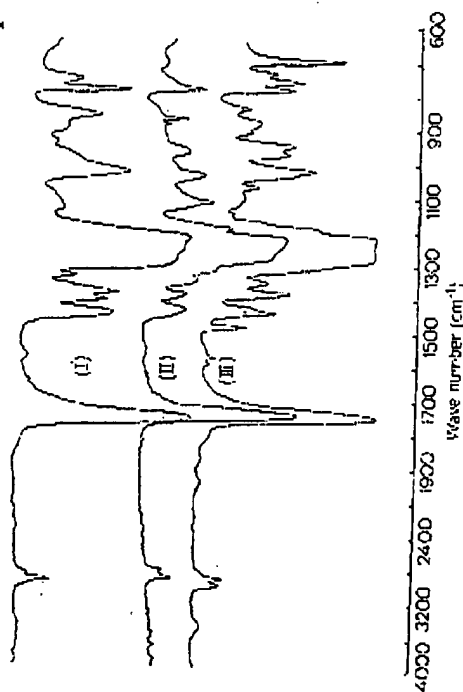


Fig. 4. IR spectra of epoxide/CO₂ copolymers. (I) EO/CO₂ copolymer (No. 43); (II) ECH/CO₂ copolymer (No. 19); (III) STO/CO₂ copolymer (No. 22)

they show strong absorptions around 1750, 1250, and 790 cm⁻¹, characteristic of the -O-CO-O- group. Moreover, the elemental analysis data of EO/CO₂ copolymer (No. 43, Found: C 40.96 H 4.88) coincides with the values calculated for poly(ethylene carbonate)



(C₃H₄O₃ requires C 40.91 H 4.54). NMR spectra of EO/CO₂ and STO/CO₂ copolymers (Fig. 5) also confirm the highly alternate structures of the copolymers. The peaks observed in the spectra taken in CDCl₃ are situated differently from those of the homopolymer of the corresponding epoxide, and they may be assigned as follows: the apparent single peak at $\tau = 5.6$ in Fig. 5-(I) is equivalent methylene protons in

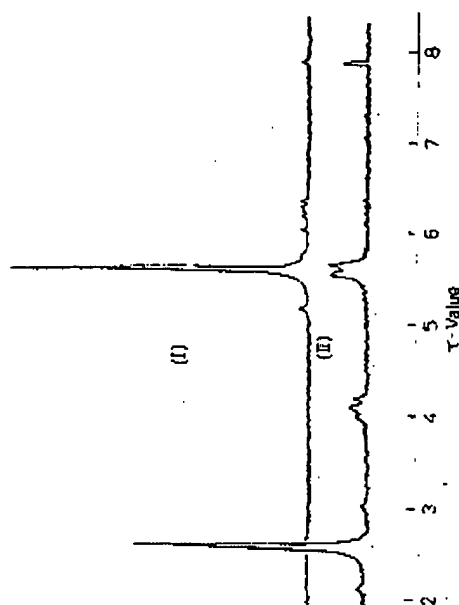
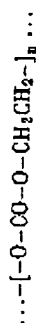


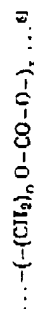
Fig. 5. NMR spectra of EO/CO₂ copolymer (I) and STO/CO₂ copolymer (II). Solvent: CDCl₃. Temp.: 56°C. Standard: Hexamethyldisiloxane

Three peaks around $\tau = 2.6$, 4.1, and 5.6 are phenyl, methine, and methylene protons in $\cdots[-\text{O}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-]_n \cdots$

respectively, and area ratios are reasonable to this assignment.

3. Thermal properties of the copolymers

Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were carried out on the copolymers of PO/CO₂ and EO/CO₂. Fig. 6 shows the results on the methanol insoluble copolymer of PO/CO₂. Both copolymers gave similar DTA-TGA curves and no remarkable changes were observed until about 180°C. In the vicinity of 200°C (a little higher in EO/CO₂ copolymer than PO/CO₂ copolymer), copolymers began to decompose with rapid decrease of weight and heat absorption. At 300°C weight became less than 10% of the starting samples. Judging from this result, melting points of the copolymers are apparently higher than those of the aliphatic polycarbonates prepared by polycondensation, since CAROTHERS *et al.* reported 50–60°C for



This difference may be thought to originate from the difference of molecular weight.

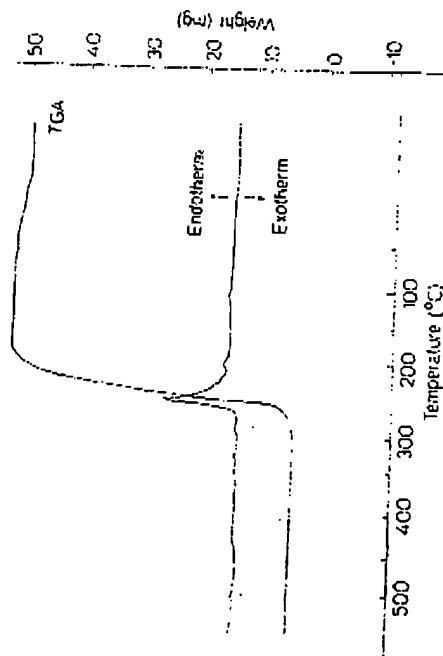


Fig. 6. DTA/TGA of PO/CO₂ copolymer (MeOH insoluble portion of No. 38). Sample: 52.5 mg. Standard: α -Al₂O₃. Temp. increase: 5°C/min. Atmosphere: N₂.

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Aus der Universität Stuttgart und dem Forschungsinstitut für Pigmente und Lacke o. V.

Untersuchungen über die anionische Polymerisation

III. Über die anionische Copolymerisation von α -Cyanosorbinsäurebutylester, 2-Nitrobuten-(1), Acrylonitril und Atropanitril*)

Von K. HÜFELMANN, R. SATTELMAYER und K. HAMANN

(Eingegangen am 11. Dezember 1967)**)

ZUSAMMENFASSUNG:

Bei der anionischen Copolymerisation von α -Cyanosorbinsäurebutylester und 2-Nitrobuten-(1) in Dimethylformamid (DMF) als Lösungsmittel waren die r -Parameter der beiden Monomeren nur wenig vom Initiatoranion und Gegenkation oder der Reaktions Temperatur abhängig. Unterschiede im Wert der Copolymerisationsparameter und im Umsatz traten bei Variation des Lösungsmittels (THF, Benzol, DMF) auf. Die Monomerenpaare α -Cyanosorbinsäurebutylester-Atropanitril und Acrylonitril-Atropanitril ergaben bei der gemeinsamen Polymerisation mit NaCN in DMF keine Copolymeren.

SUMMARY:

In the anionic copolymerization of α -cyanosorbic acid butylester with 2-nitrobutene-(1) in DMF as solvent the anion of initiator, the counter ion and the temperature of reaction showed no marked influence on the copolymerization parameters. Different r values and yields were found in varying the solvent (THF, benzene, DMF). No copolymers were obtained by polymerization of the monomer pairs α -cyanosorbic acid butylester- α -cyanostyrene and α -cyanostyrene-acrylonitrile with NaCN in DMF.

1. Einleitung

In einer früheren Arbeit¹⁾ wurde von R. SATTELMAYER und K. HAMANN über die Abstufung der Reaktionsfähigkeit stark aktivierter Monomere bei der anionischen Copolymerisation berichtet. Für die Abstufung der Reaktionsfähigkeit der untersuchten Monomeren konnte die folgende Reihe aufgestellt werden:

Methylenmalonester : 2-Nitropropen : α -Cyanosorbinsäurebutylester : 1-Nitropropen \approx β -Nitrostyrol : Acrylonitril.

In dieser Arbeit wird die obige Reaktivitätsreihe von Monomeren, die nach dem anionischen Mechanismus copolymerisieren, um weniger akti-

*) H. MÜLLER, K. HÜFELMANN, R. SATTELMAYER und K. HAMANN, *Makromolekulare Chem.* **112** (1968) 301.

**) Revidierte Fassung vom 11. August 1969.

W. Kuran, S. Pasynkiewicz, J. Skupińska, and A. Rokicki

Weiterhin wurde die Copolymerisation von CO_2 und PO in Gegenwart des Systems $(\text{C}_2\text{H}_5)_2\text{Zn}/\text{Resorcin}$ (1:1, mol/mol) bei verschiedenen Temperaturen und in Reaktionsmedien unterschiedlicher Basizität untersucht.

Auf Grund der erhaltenen Ergebnisse der Copolymerisation von CO_2 mit PO und der Messung des sich in den Reaktionen zwischen den Katalysatorkomponenten entwickelnden Äthanvolumens, werden Strukturen verschiedener Katalysatoren, insbesondere der homogenen, vorgeschlagen und einige Aspekte des Copolymerisationsmechanismus diskutiert.

Introduction

The alternating copolymerization of carbon dioxide and epoxides leading to the formation of high-molecular polycarbonates has been described in the literature¹⁻⁸. In the copolymerization of CO_2 with propylene oxide, (1,2-diepoxpropane), (PO), diethylzinc/water¹⁻³, primary amine³, dihydric phenol or naphthol^{6,7}, benzenedicarboxylic acid or hydroxybenzoic acid⁸, and aliphatic dicarboxylic acid⁹ systems are effective as catalysts.

This paper describes new catalytic systems for the alternating copolymerization of CO_2 and PO: diethylzinc/trihydric phenols or aminophenols. Copolymerization reactions were carried out with these systems and, for comparison, with other systems in order to explain some aspects of the catalyst's structure and copolymerization mechanism.

Also the influence of temperature and type of solvent on the copolymerization reaction of CO_2 with PO carried out in the presence of the diethylzinc/resorcinol (1:1 by mole) system, described in the literature^{6,7}, was examined.

Experimental Part

Materials

Diethylzinc and triethylaluminium (commercial grade reactants) were dist. before use in nitrogen atmosphere. Diethylmagnesium was obtained according to a procedure reported in the literature².

Propylene oxide, (PO), (commercial grade reactant) was dried and dist. over calcium hydride in nitrogen atmosphere. Commercial grade CO_2 was used without further purification.

The solvents and reagents used as cocatalysts were purified according to known procedures.

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four coordination positions permanently occupied, the catalytic activity is low.

The active catalyst's centres having, due to association, free coordination positions, can be occupied by solvent or monomer molecules. Our investigations on the influence of the reaction medium on the copolymer yield show that, when the catalyst is complexed with such a strong base as pyridine, the copolymerization is inhibited.

Decreasing the solvent basicity, we found a remarkable increase in the yield of the copolymer being highest for diethyl carbonate. Besides the influence of the solvent basicity¹⁰ on the copolymer's yield, also a considerable influence of the solubility of carbon dioxide in the solvents is observed; it decreases in the following series¹¹: diethyl carbonate > ethers > pyridine > benzene > chlorohydrocarbons.

A low yield of copolymer in the reaction carried out in a mixture of solvents (1,4-dioxane/benzene, *c.* Tab. 2) is due to a lower concentration of carbon dioxide in the reaction medium.

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New Catalytic Systems for the Fixation of Carbon Dioxide. 1. Copolymerization of CO₂ and Propylene Oxide with New Rare-Earth Catalysts—RE(P₂₀₄)₃—Al(*i*-Bu)₃—R(OH)_{*n*}

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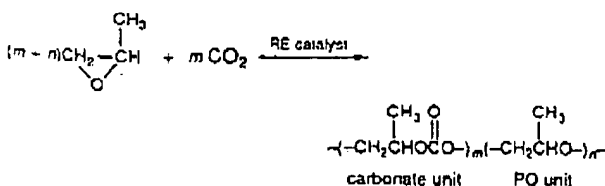
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ABSTRACT: Copolymerization of propylene oxide and carbon dioxide was successfully carried out by using new rare-earth catalytic systems for the first time. It has been found that ternary rare-earth coordination catalysts composed of rare-earth phosphonate, triisobutylaluminum, and glycerine are effective catalysts for the copolymerization. The system Y(P₂₀₄)₃—Al(*i*-Bu)₃—glycerine shows the highest activity. The yield and intrinsic viscosity of the copolymer depend significantly on the molar ratio of catalyst components and the reaction condition. The copolymers prepared were characterized by IR, ¹H NMR, GPC, and DTA-TGA. It is shown that the copolymers obtained have a high molecular weight with a narrow molecular weight distribution and a high thermal stability. The carbonate unit content of the methanol-insoluble copolymer is as high as 30–40%.

Chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization and environmental problems. As a kind of catalytic fixation of carbon dioxide, copolymerization reactions of carbon dioxide with various epoxides have been investigated extensively in recent years. The effective catalysts reported so far for the copolymerization consist of diethylzinc and compounds with active hydrogen, such as water,¹ primary amine,² di- or trihydric phenol,³ dicarboxylic acid,⁴ polymer,⁵ etc. However, the yield and molecular weight of the copolymer are still to be improved.

Recently, we have found that rare-earth coordination catalysts are very effective catalysts for the ring-opening polymerization or copolymerization of alkylene oxide and sulfide, such as ethylene oxide,⁶ propylene oxide,⁷ epichlorohydrin,⁸ and propylene sulfide,⁹ giving high molecular weight polymers with a high rate. In this paper, the exploitation of new catalysts composed of rare-earth compounds for the copolymerization of carbon dioxide with propylene oxide (PO) has been reported for the first time. The catalytic systems, especially Y(P₂₀₄)₃—Al(*i*-Bu)₃—glycerine, give a high yield within a short time. Also, the copolymers obtained are random copolymers with a high molecular weight, a narrow molecular weight distribution, and a high thermal stability:



Experimental Section

Materials. Propylene oxide, 1,4-dioxane, toluene, and other solvents were purified by the usual methods before use. Commercial carbon dioxide (purity more than 99.9%) was used without further purification. Rare-earth complexes RE(P₂₀₄)₃ (RE = La, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y; P₂₀₄ = (RO)₂P(O)O—, R = CH₂(CH₂)₃CH(C₂H₅)CH₂) were prepared by using the method described in ref 10. A toluene solution of RE(P₂₀₄)₃—Al(*i*-Bu)₃ was prepared according to ref 6. The catalysts RE(P₂₀₄)₃—Al(*i*-Bu)₃—III were obtained under a nitrogen atmosphere by dropwise addition a 1,4-dioxane solution

of the third component (III) into the solution of RE(P₂₀₄)₃—Al(*i*-Bu)₃.

Copolymerization. Copolymerization of carbon dioxide with PO was carried out in a 80-mL stainless steel autoclave. After the reaction was completed, the reaction mixture was terminated with methanol containing 5% hydrochloric acid. The resulting copolymer was precipitated by water, washed with water several times, and then dried in vacuo at room temperature.

Analysis of Copolymer. The ¹H NMR spectra of the copolymer in deuteriochloroform were measured at room temperature with a JEOL FX-90Q NMR spectrometer using tetramethylsilane (TMS) as the internal reference. The carbonate unit content of the copolymer (CU %) was calculated from the area ratio of peaks at 5.0, 4.2, and 3.5 ppm in the ¹H NMR spectrum according to the following equation:

$$\text{CU \%} = \frac{A_{5.0} + A_{4.2}}{A_{5.0} + A_{4.2} + A_{3.5}}$$

IR spectra of the copolymer films were recorded on a Nicolet 5D FTIR spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters 208 LC/GPC equipped with a differential refractometer detector by using polystyrene (MW = 2350–1.2 × 10⁶) as the standard. The thermal property of the copolymer was measured with a DT-30 calorimeter. The intrinsic viscosity of the copolymer was measured in benzene at 35 °C by using an Ubbelohde viscometer. The number-average molecular weight of the copolymer was calculated according to the following equation:¹¹

$$[\eta] \text{ (dL/g)} = 1.11 \times 10^{-4} M_n^{0.8}$$

Results and Discussion

Copolymerization of CO₂ and PO with Various Rare-Earth Systems. Combinations of 14 rare-earth phosphonates, RE(P₂₀₄)₃, with Al(*i*-Bu)₃ and glycerine were used as catalysts for the copolymerization of carbon dioxide and PO. The results are summarized in Table I. It has been found that all these rare-earth coordination catalysts are effective catalysts for the fixation of CO₂, but the Y(P₂₀₄)₃—Al(*i*-Bu)₃—glycerine system is the most outstanding catalyst among the combinations tested, because it gives both a high yield and a high molecular weight copolymer. So the studies were focused on the Y catalyst systems. The reason for yttrium and lutetium systems showing a higher activity probably is that their electronic structures are more appropriate for the active species formation.

Table I
Copolymerization of PO and CO₂ with
Re(P₂₀₄)₃-Al(*i*-Bu)₃-Glycerine^a

RE	yield, g/mol of Y	[η], dL/g	$\bar{M}_n \times 10^{-4}$
Sc	1223	0.315	2.07
Y	1672	3.82	46.9
La	897	0.485	3.55
Nd	973	0.417	2.94
Eu	855	1.04	9.22
Gd	552	0.210	1.25
Tb	894	0.093	0.45
Dy	934	1.00	8.78
Ho	1289	0.545	4.12
Er	473	0.330	2.20
Tm	158	0.690	5.52
Yb	1210	0.600	6.63
Lu	1526	1.87	16.7

^a Al/RE = 8; III/Al = 0.5; [PO] = 2.15 mol/L; 30–40 atm of CO₂; 17 h; 60 °C; (RE) = 0.038 mol/L; 1,4-dioxane + toluene (4:1) as solvent.

Table II
Effect of the Structure of Component III on Catalytic Activity^a

no.	III	yield	[η], dL/g	$\bar{M}_n \times 10^{-4}$
1	H ₂ O	1052	1.58	15.6
2	CH ₃ OH	295	1.19	10.9
3	HOCH ₂ CH ₂ OH	715	0.73	5.9
4	glycerine	2451	3.87	47.6
5	2-propanol	421	0.69	5.5
6	<i>n</i> -C ₄ H ₉ OH	515	1.02	9.0
7	(CH ₃) ₂ COH	663	1.13	10.2
8	propylene glycol	263	0.89	7.6
9	2-butyn-1,4-diol	842	2.03	21.3
10	CH ₃ OH/glycerine (1:1)	552	2.01	21.0
11	glycerine/CH ₃ OH (1:1)	842	2.54	28.1
12	CH ₃ OH/glycerine/CH ₃ OH (1:2:1)	1197	3.44	41.1

^a Al/Y = 8; III/Al = 0.5; [PO] = 2.15 mol/L; 30–40 atm of CO₂; 60 °C; 16 h; dioxane. Nos. 1–8: (Y) = 4.76 × 10⁻² mol/L. Nos. 9–12: (Y) = 3.8 × 10⁻² mol/L.

Effect of the Structure of Component III on Catalytic Activity. It has been found that the catalytic activity appeared to be strongly dependent on the nature of the third component of the rare-earth catalyst. Table II illustrates the results of the effect of various III components on the copolymerization of PO and carbon dioxide with the Y(P₂₀₄)₃-Al(*i*-Bu)₃ system. All of the catalyst systems tested seemed to be active for the copolymerization of PO and carbon dioxide. The products obtained are random copolymers, with a carbonate unit content from 10% to 30% having a structure of polycarbonate with some ether linkage (characterized by IR and ¹H NMR). It was noteworthy that the Y(P₂₀₄)₃-Al(*i*-Bu)₃-glycerine system showed the highest activity in the copolymerization reaction, giving a high yield as well as a high molecular weight copolymer. It is reasonable to assume that glycerine might incorporate into the active species, as in the case of the zinc system.¹²

Characteristics of the Copolymerization with Y-(P₂₀₄)₃-Al(*i*-Bu)₃-Glycerine. The catalyst component ratios of the Y(P₂₀₄)₃-Al(*i*-Bu)₃-glycerine system are the most important factors influencing the copolymerization of PO and carbon dioxide. Figures 1, 2 present the dependence of the copolymer yield and intrinsic viscosity on the molar ratio of the catalyst components, i.e., Al/Y and glycerine/Al molar ratios. It is seen from Figure 1 that the copolymer yield and intrinsic viscosity both increase with an increase of the Al/Y molar ratio, and the intrinsic viscosity of the copolymer attains a maximum value. The optimum Al/Y molar ratio for the copoly-

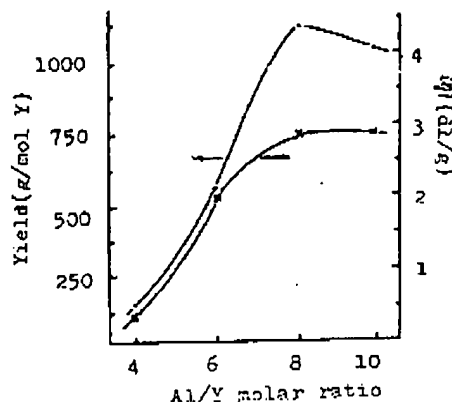


Figure 1. Effect of Al/Y molar ratio on copolymerization. Conditions: III/Al = 0.5; [Y] = 4.76 × 10⁻² mol/L; [PO] = 2.15 mol/L; 30–40 atm of CO₂; 60 °C; 10 h; 1,4-dioxane + toluene (4:1) as solvent.

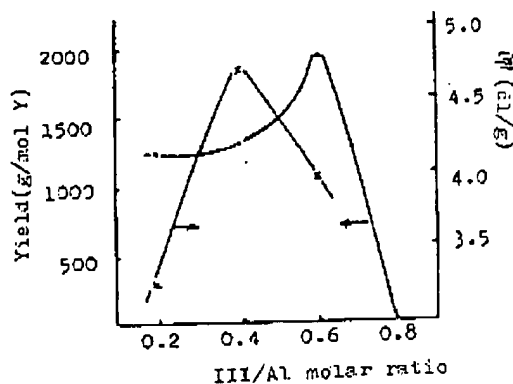


Figure 2. Effect of glycerine/Al molar ratio on the copolymerization. Conditions: Al/Y = 8; [Y] = 4.76 × 10⁻² mol/L; [PO] = 2.15 mol/L; 30–40 atm of CO₂; 60 °C; 16 h; 1,4-dioxane + toluene (4:1) as solvent.

erization is 8. It seems that a kind of bimetallic species formed at Al/Y = 8 involving Al and Y is responsible for the high yield and high molecular weight of the copolymer. Figure 2 indicates that both the copolymer yield and the intrinsic viscosity have maximum values at 0.6 and 0.4 glycerine/Al molar ratios, respectively. The highest intrinsic viscosity reaches 4.73 dL/g ($\bar{M}_n = 61 \times 10^4$). It seems that an excess amount of glycerine might destroy the bimetallic catalyst species, thus decreasing the yield and [η].

Figure 3 shows the effect of catalyst concentration on the copolymerization, retaining other conditions: [PO] = 2.15 mol/L, Al/Y = 8, III/Al = 0.5, 30–40 atm CO₂, 60 °C, 18 h. It has been found that the yield and intrinsic viscosity of the copolymer increase rapidly with an increase of the catalyst concentration when [Y] is from 2.6 × 10⁻² to 3.9 × 10⁻² mol/L. The most favorable catalyst concentration is in the range of 3.8 × 10⁻²–5.7 × 10⁻² mol/L.

The Y(P₂₀₄)₃-Al(*i*-Bu)₃-glycerine system exhibited a pattern of the reaction time dependence of the copolymer yield and molecular weight similar to that of other systems reported.¹³ During the reaction, both the yield and the molecular weight of the copolymer increased with an increase of the reaction time to a maximum (Figure 4). This agrees with an anionic coordinate polymerization mechanism.¹³ A little drop of the intrinsic viscosity of the copolymer at more than 40 h was probably due to the copolymer degradation in the presence of catalyst as reported by Kuran.¹⁴

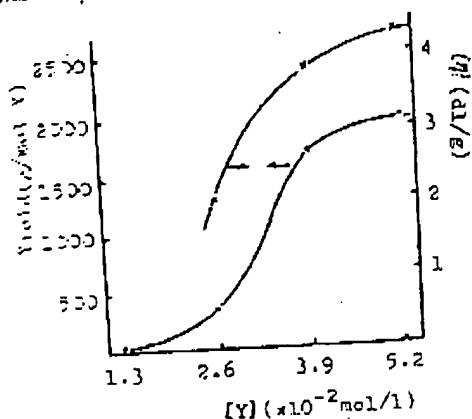


Figure 3. Effect of catalyst concentration on the copolymerization. Conditions: Al/Y = 8; glycerine/Al = 0.5; [PO] = 2.15 mol/L; 30–40 atm of CO₂; 60 °C; 18 h; 1,4-dioxane + toluene (4:1) as solvent.

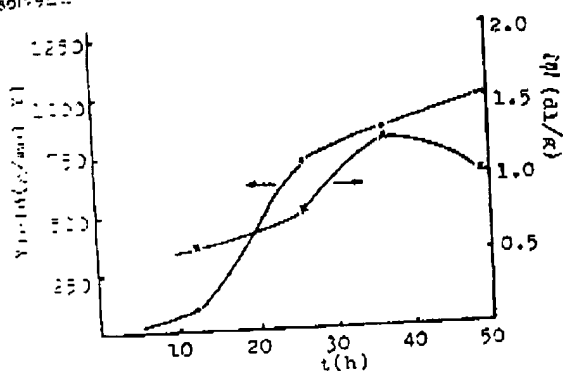


Figure 4. Reaction time dependence of the copolymer yield and the intrinsic viscosity. Conditions: 20 °C; [PO] = 2.15 mol/L; 30–40 atm of CO₂; [Y] = 3.8 × 10⁻² mol/L; Al/Y = 8; III/Al = 0.5; 1,4-dioxane + toluene (4:1) as solvent.

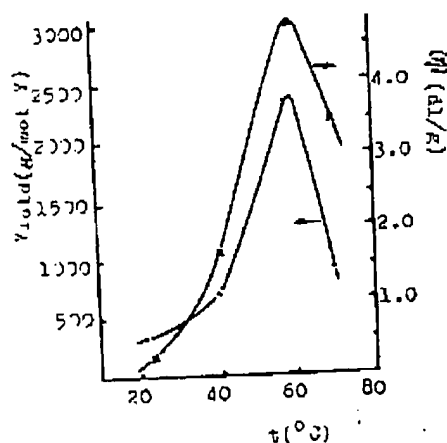


Figure 5. Influence of reaction temperature on the yield and [η] of copolymer. Conditions: Al/Y = 8; III/Al = 0.5; [Y] = 3.8 × 10⁻² mol/L; 24 h; 30–40 atm of CO₂; [PO] = 2.15 mol/L; 1,4-dioxane + toluene (4:1) as solvent.

The effect of reaction temperature on the copolymerization is illustrated in Figure 5. Both the yield and the intrinsic viscosity of the copolymer have maximum values at 60 °C. The decrease of the yield and the intrinsic viscosity of the copolymer at more than 60 °C may be caused by the depolymerization and degradation of the copolymer.¹³

Table III
Copolymerization of PO with CO₂ in Different Solvents by Using Y(P₂O)₃-Al(*i*-Bu)₃-Glycerine as Catalyst^a

no.	solvent	yield, g/mol of Y	[η], dL/g
1	benzene	1420	2.95
2	THF	302	0.37
3	ether	329	0.88
4	2-butanone	no polymer	
5	DMF	no polymer	
6	cyclohexane	1986	2.75
7	petroleum benzin	1670	2.75
8	toluene	3064	1.07
9	CH ₂ Cl ₂	trace	
10	1,4-dioxane/benzene (1:1)	3274	0.94

^a Al/Y = 8; III/Al = 0.5; [Y] = 3.8 × 10⁻² mol/L; [PO] = 2.15 mol/L; 17 h; 60 °C; 30–40 atm of CO₂.

Table IV
Some Properties of Three Specimens with Different Intrinsic Viscosities

sample ^a	percentage, %	[η], dL/g	CU %	GPC ^b data		
				$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	MWD
1		3.82		39.6	85.2	2.15
1 (S)	57			28.9	72.8	2.52
1 (I)	43		33	70.6	112.4	1.59
2		4.28		43.9	86.2	1.96
2 (S)	54			21.8	68.3	3.13
2 (I)	46		30	77.3	118.4	1.53
3		4.82		79.6	116.3	1.46
3 (S)	28			62.0	109.8	1.77
3 (I)	72		ca. 30	79.9	122.9	1.54

^a S, methanol-soluble; I, methanol-insoluble. ^b All of the GPC curves have only one peak; measured at 30 °C; THF as eluent.

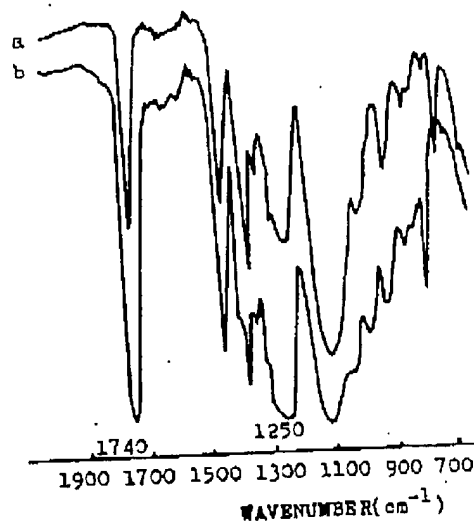


Figure 6. IR spectra of the copolymer: (a) methanol-soluble part; (b) methanol-insoluble part.

The copolymerization of PO and carbon dioxide can also be carried out in other solvents. The yield of the copolymer was greatly influenced by the solvent used, as shown in Table III. The activity sequence is as follows: 1,4-dioxane/benzene (1:1) > toluene > aliphatic hydrocarbon > ether, THF > CH₂Cl₂ > DMF, 2-butanone. This might be related to the solubility of CO₂ in various solvents. The structure of the copolymer was also influenced by the solvent used and the polymerization temperature.

In conclusion, the rare-earth coordination catalysts composed of RE(P₂O)₃, Al(*i*-Bu)₃, and glycerine are effective for the copolymerization of carbon dioxide and PO. The highest yield and intrinsic viscosity of the

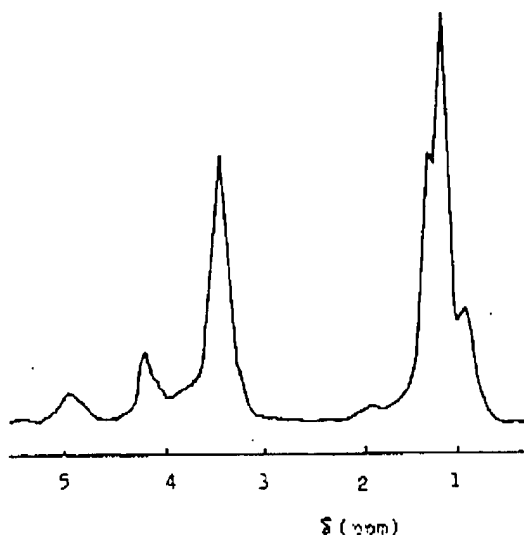


Figure 7. ^1H NMR spectrum of the methanol-insoluble copolymer.

copolymer reach more than 3000 g/mol of Y and 4.73 dL/g ($M_n = 61 \times 10^4$), respectively. The most favorable conditions for the copolymerization of CO_2 and PO catalyzed by the $\text{Y}(\text{P}_{204})_3\text{-Al}(\text{i-Bu})_3$ -glycerine system are as follows: $\text{Al/Y} = 8$; $\text{III/Al} = 0.4\text{--}0.6$; 60°C ; 1,4-dioxane/benzene, 1,4-dioxane/toluene, or 1,4-dioxane as solvent.

Characterization of the CO_2/PO Copolymer. The rare-earth copolymers obtained have a high molecular weight and a narrow molecular weight distribution. Table IV illustrates some properties of three typical specimens with different intrinsic viscosities. The data show that the copolymers are partly insoluble in methanol (40–75%). It has been found that the molecular weight and the carbonate unit content (CU %) of the methanol-insoluble portions are higher than those of the methanol-soluble portions. The IR spectra of the two parts are shown in Figure 6. Strong absorption bands at 1740 and 1250 cm^{-1} are due to the C=O and C-O stretching vibrations of the oxycarbonyloxy group, respectively.

The ^1H NMR spectrum (Figure 7) of the methanol-insoluble part shows chemical shifts from internal TMS at 1.3 ppm for CH_3 , 3.5 ppm for $\text{CH} + \text{CH}_2$ in the PO unit, 4.2 ppm for CH_2 in the carbonate unit, and 5.0 ppm for CH in the carbonate unit. The carbonate unit content of the methanol-insoluble copolymer calculated from the ^1H NMR is in the range of 30–40%.

DTA-TGA analysis shows that the copolymers obtained are highly thermally stable. The decomposition temperature is more than 300°C (Figure 8).

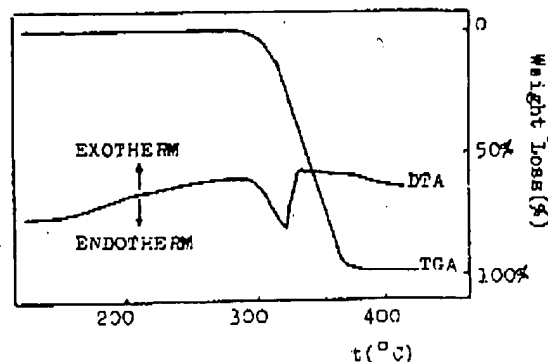


Figure 8. DTA-TGA analysis of the copolymer N_2 ; 10°C/min .

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Registry No. (PO)(CO_2) (copolymer), 25511-85-7; $\text{Sc}(\text{P}_{204})_3$, 22989-17-9; $\text{Y}(\text{P}_{204})_3$, 38326-06-6; $\text{La}(\text{P}_{204})_3$, 45324-95-6; $\text{Nd}(\text{P}_{204})_3$, 38326-04-4; $\text{Eu}(\text{P}_{204})_3$, 79950-28-0; $\text{Gd}(\text{P}_{204})_3$, 79950-29-1; $\text{Tb}(\text{P}_{204})_3$, 79950-30-4; $\text{Dy}(\text{P}_{204})_3$, 45324-92-3; $\text{Ho}(\text{P}_{204})_3$, 45324-94-5; $\text{Er}(\text{P}_{204})_3$, 79950-31-5; $\text{Tm}(\text{P}_{204})_3$, 26312-52-7; $\text{Yb}(\text{P}_{204})_3$, 38326-05-5; $\text{Lu}(\text{P}_{204})_3$, 79950-32-6; $\text{Al}(\text{i-Bu})_3$, 100-99-2; H_2O , 7732-18-5; CH_3OH , 67-56-1; $\text{HO}(\text{CH}_2)_2\text{OH}$, 107-21-1; $\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$, 67-63-1; $n\text{-C}_4\text{H}_9\text{OH}$, 71-36-3; $(\text{CH}_3)_2\text{COH}$, 75-65-0; $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$, 110-65-6; propylene glycol, 57-55-6; glycerine, 56-81-5; benzene, 71-43-2; tetrahydrofuran, 109-99-9; cyclohexane, 110-82-7; toluene, 108-88-3; 1,4-dioxane, 123-91-1; ether, 60-29-7.

Catalytic Reactions Involving C_1 Feedstocks: New High-Activity Zn(II)-Based Catalysts for the Alternating Copolymerization of Carbon Dioxide and Epoxides

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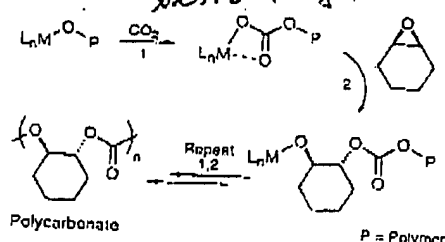
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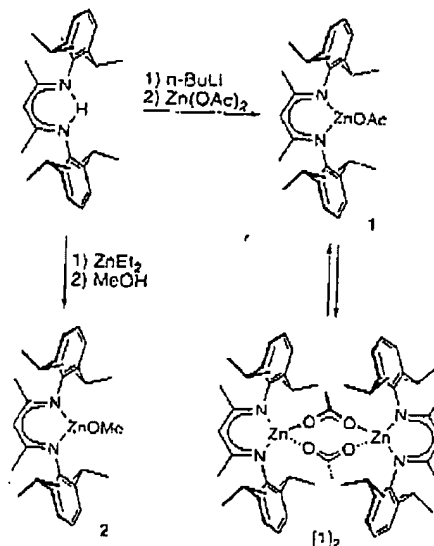
Carbon dioxide is an ideal synthetic feedstock since it is abundant, inexpensive, nontoxic, and nonflammable. Although it is estimated that Nature uses CO_2 to make over 200 billion tons of glucose by photosynthesis each year,¹ synthetic chemists have had little success in developing efficient catalytic processes that exploit this attractive raw material.² There has been considerable recent interest in the development of catalysts for the alternating copolymerization of carbon dioxide with epoxides to produce aliphatic polycarbonates.³ Because of the low cost and accessibility of the monomers and the attractive properties of polycarbonates, the development of new, efficient initiators for this polymerization process is a significant scientific goal.^{4–10} We report here a new class of well-defined, high-activity Zn(II) catalysts that copolymerize carbon dioxide and epoxides under exceptionally mild conditions.

The proposed mechanism of the copolymerization reaction is depicted in Scheme 1.¹¹ Repetition of the sequence in which CO_2 inserts into a metal alkoxide, followed by epoxide ring-opening with the metal carbonate forms the alternating copolymer. Two catalytic systems have been recently discovered that, prior to the present work, were the most active reported zinc-based systems for CO_2 /epoxide polymerization. Darensbourg and Holtcamp have reported novel Zn(II) bis(2,6-diphenylphenoxide) initiators for the copolymerization of CO_2 and epoxides.¹² Immediately after initiation, it is probable that the remaining bulky phenoxide ligand of the complex prevents aggregation yet allows monomer coordination. Beckman et al. have developed a highly active Zn-based compound for cyclohexene oxide (CHO) copolymerization in supercritical CO_2 .^{13,14} The key to success in this system was a

Scheme 1



Scheme 2



fluorinated carboxylate ligand that provided catalyst solubility in supercritical CO_2 . In each of these systems, it is vital that the monomer does not displace the ligand from the active site during the polymerization reaction. On the basis of this lead, we investigated the synthesis and application of Zn(II) complexes incorporating chelating, bulky β -diimine ligands¹⁵ as catalysts for epoxide/ CO_2 copolymerization.

Deprotonation of the β -diimine ligand (BDI-H, derived from 2,6-diisopropylaniline)¹⁶ with *n*-butyllithium and subsequent reaction with zinc acetate yields [(BDI)Zn(OAc)] (1) (Scheme 2).¹⁷ Reaction of BDI-H with $ZnEt_2$ gives [(BDI)ZnEt] which produces [(BDI)Zn(OMe)] (2) upon reaction with methanol. The X-ray crystal structure of 1¹⁸ is shown in Figure 1; the structure reveals a tetrahedral zinc center and aryl groups that are approximately perpendicular to the plane of the N–Zn–N chelate. Complex 1 exists as the acetate-bridged dimer in the solid-state. The ¹H NMR spectrum of 1 in benzene-*d*₆ (1×10^{-2} M) exhibits two sets of shifts whose intensities vary with concentration; the set that becomes more intense as concentration decreases was assigned

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Syntheses and Structures of Epoxide Adducts of Soluble Cadmium(II) Carboxylates. Models for the Initiation Process in Epoxide/CO₂ Coupling Reactions

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Dicarboxylates of zinc(II) afford the most active catalysts to date for the copolymerization of CO₂ and epoxides to produce high molecular weight polycarbonates.^{1,2} This polymerization process represents one of the few examples of an economically feasible catalytic incorporation of CO₂ into useful organic products.³ Nevertheless, it is only marginally practical, suffering from such factors as low polymer yields and reproducibility, side reactions which afford cyclic carbonates, and the use of environmentally unfavorable solvents. This latter deficiency has been partially mitigated via the employment of supercritical carbon dioxide as both solvent and reactant.⁴ More importantly, mechanistic investigations have been frustrated largely due to difficulties in assessing the nature of these heterogeneous catalysts.⁵ Significant mechanistic studies are necessary in order to provide a better understanding of the intimate reactions involved in this process and, hence, improve its utility. This report describes the use of Cd(II) carboxylates, solubilized in organic solvents by the tris-3-phenylpyrazole hydroborate ligand,⁶ as model reagents for the heterogeneous catalytic system. In particular the reactions of these carboxylate derivatives with epoxides to afford novel, isolable metal-epoxide complexes and their subsequent reactions to provide C-O bonds will be presented.

The ¹¹³Cd nucleus being NMR active provides a highly sensitive spectroscopic probe for observation of its reaction chemistry.⁷ Indeed, substitution of Zn(II) with Cd(II) has been used extensively to study zinc enzymes.⁸ (η^3 -HB(3-Phpz)₃)-Cd(II)(acetate)-THF may be prepared by the addition of slightly less than 1 equiv of K[η^3 -HB(3-Phpz)₃] to Cd(acetate)₂ in THF.

Addition of H₂O results in the precipitation of product in high yields. One equivalent of THF per Cd ion was found in the resulting complex as verified by ¹H NMR and chemical analysis.⁹ ¹¹³Cd NMR indicated total dissociation of the THF adduct in chloroform or dichloromethane at room temperature as observed by a single resonance at 150 ppm relative to Cd-(ClO₄)₂. The saturated six-coordinate species was observed at a resonance of 83.4 ppm at -90 °C in dichloromethane in the presence of excess THF.¹⁰

The observation of a labile THF at the Cd(II) center suggests the possibility of preparing a Cd(II) carboxylate complex with a coordinated epoxide ligand. Indeed, we have been able to isolate the corresponding propylene oxide and cyclohexene oxide derivatives (1 and 2, respectively) by a repeated dissolution of the THF complex in the epoxide solvent.¹¹ Because of the unusual nature of these complexes, we have characterized them by single-crystal X-ray diffraction.¹² The molecular structures of these complexes are depicted in Figures 1 and 2. Although the structure of a ruthenium(II) thirane complex has been published,¹³ only recently has the first crystal structure of a metal epoxide complex been reported for a ruthenium porphyrin derivative of styrene oxide.¹⁴ One-to-one adducts of epoxides with Cd(II) porphyrins have been observed spectrophotometrically; however, to our knowledge the complexes presented herein represent the only other structurally characterized examples containing metal-epoxide binding.¹⁵ In contrast to analogous Zn(II) carboxylates, which typically are four- or five-coordinate with unidentate or asymmetrically chelated carboxylate ligands,¹⁶ these Cd(II) derivatives are six-coordinate with the acetate being rather symmetrically bonded to the metal

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Alternating Copolymerization of Carbon Dioxide and Propylene Oxide with a Rare-Earth-Metal Coordination Catalyst

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ABSTRACT: The copolymerization of carbon dioxide and propylene oxide using rare-earth-metal catalyst systems was investigated in this study. It was found that the ternary rare-earth-metal coordination catalyst consisting of $Y(CF_3CO_2)_3$ (I), diethylzinc (II), and glycerine (III) was the most effective catalyst system to generate an alternating polycarbonate. The effects of the molar ratio of catalyst components, the solvent, and the operating temperature and pressure on the yield and the molecular weight of polycarbonate were systematically studied. At an appropriate combination of all variables, the yield could be as high as 4200 (g/(mol of Y))/h and the molecular weight as high as 1.0×10^5 in a 12 h reaction period. The carbonate content in the resulting polycarbonate was found to be 95.6%.

Introduction

Carbon dioxide is a known greenhouse gas which contributes over half of the greenhouse effect. The necessity to reduce CO_2 emission has gained the consent of most of the countries in the world. One of the means to reduce CO_2 emission is to use CO_2 as a starting material in chemical reactions. In addition to environmental concerns, CO_2 may become a very important raw material in chemical industry in the future, since the sources of coal, petroleum, and natural gas are being quickly exhausted and the carbon content of CO_2 in the atmosphere and in the hydrosphere is by $1\frac{1}{2}$ orders of magnitude more than that in coal, petroleum, and gas.¹

Generally CO_2 is thought of as an inert and relatively unreactive compound; there is no report so far on the homopolymerization of CO_2 . However, in 1969, Inoue et al.² observed that the copolymerization of CO_2 with epoxide could proceed to form polycarbonate using organometallic compounds as catalysts under relatively mild conditions. Since then, many attempts to develop new catalysts and to copolymerize other monomers with CO_2 have been made, which are described in the excellent reviews of Rokicki and Kuran,³ Scholsky,⁴ and Yamazaki et al.⁵

In the copolymerization reaction of CO_2 with propylene oxide (PO), the effective organometallic catalysts for producing an alternating polycarbonate were found to consist of diethylzinc and a compound having two active hydrogens, such as water,⁶ primary amines,⁷ di- or trihydroxybenzenes,⁸⁻¹⁰ aromatic dicarboxylic acids,¹¹⁻¹³ polymers,¹⁴ etc. However, to carry out this copolymerization reaction, a long reaction time is generally required, and the yield needs to be improved. The reaction mechanism for this kind of catalyst system has been identified as an anionic coordination process.¹¹

Recently, Chen et al.¹⁵ successively carried out the copolymerization of CO_2 and propylene oxide by using a rare-earth-metal catalyst system. They found that the ternary rare-earth-metal coordination system $Y(P_{204})_3$ - $Al(i-Bu)_3$ -glycerine is the most effective catalyst for the reaction. Despite the fact that random copolymers of polycarbonate were obtained, a higher molecular weight with a narrower molecular weight distribution and a

higher yield within a shorter reaction time compared with the previous organometallic compound catalyst systems were observed in their study.

Since an alternating polycarbonate has its special application, the objective of this study is to produce it from the copolymerization of CO_2 and PO by using the rare-earth-metal catalyst systems. As shown in the literature, diethylzinc in organometallic compound systems can generate more alternating copolymers than triisobutylaluminum does.^{2,15} Therefore, diethylzinc instead of triisobutylaluminum was employed in the present rare-earth-metal catalyst systems. In addition to $Y(P_{204})_3$, the rare-earth-metal compounds $Y(CH_3CO_2)_3$ and $Y(CF_3CO_2)_3$ were also used. It has been shown that $Y(CF_3CO_2)_3$ is an effective catalyst for the ring opening of tetrahydrofuran (THF) in the polymerization of THF.¹⁶ In this study, the effects of pressure and temperature on yield and molecular weight were also examined.

Experimental Section

Materials. Propylene oxide of a purity of 99.5% (Janssen Chimica) was refluxed over CaH_2 and 4A molecular sieves and was distilled before use. Diethylzinc, glycerine, and all of the solvents, such as *n*-hexane, benzene, toluene, DMSO, and 1,3-dioxolane, were of analytical reagent grade and were used without further purification. CO_2 of a purity higher than 99.99% (Air Product Co.) was used as received. $Y(P_{204})_3$ was prepared as follows: YCl_3 was first produced from an aqueous solution containing 0.01 mol of Y_2O_3 and 0.06 mol of HCl at 100 °C, and then 0.03 mol of phosphoric acid bis(2-ethylhexyl) ester was added into the resulting YCl_3 solution at room temperature to produce $Y(P_{204})_3$. The resultant $Y(P_{204})_3$, $Y(CF_3CO_2)_3$, and $Y(CH_3CO_2)_3$ purchased from Aldrich Chemical Co. were heated in vacuum at 80 °C for 40 h before use.

The catalyst system $Y(CF_3CO_2)_3$ - $Zn(Et)_2$ -glycerine was prepared in an atmosphere of purified argon. Glycerine was added dropwise to a solution of $Zn(Et)_2$ in solvent at room temperature. After ethane gas evolution had ceased, the solution containing white powders resulting from the reaction between $Zn(Et)_2$ and glycerine was heated at 60 °C for 2 h. This solution was then added to an autoclave which contained a known amount of $Y(CF_3CO_2)_3$. The resultant catalyst was stirred at 60 °C for 1 h prior to CO_2 and PO being introduced.

Copolymerization. Copolymerization of CO_2 and PO was carried out in a 300 mL autoclave which was equipped with a magnetic stirrer (Autoclave Engineers Inc.). The spinning

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Table 1. Copolymerization of CO₂ and PO by Various Catalysts^a

catalyst system			yield, (g/mol of Y)/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
I	II	III				
Y(CF ₃ CO ₂) ₃	Zn(Et) ₂	glycerine	1600	3.0	1.2	4.00
Y(CF ₃ CO ₂) ₃	Zn(Et) ₂	trace	trace			
Y(CF ₃ CO ₂) ₃	Zn(Et) ₂	glycerine	80	3.5	1.35	3.85
Y(CF ₃ CO ₂) ₃	Zn(Et) ₂	PO	Trace			
Y(P ₂₀₄) ₃	Zn(Et) ₂	glycerine	170	4.7	2.0	4.26
Y(CH ₃ CO ₂) ₃	Zn(Et) ₂	glycerine	Trace			

^a I = 0.00055 mol; II = 0.011 mol; III = 0.0055 mol; solvent = 20 mL of toluene; PO = 30 mL; T = 60 °C; P = 400 psi; time = 6 h.

speed was kept at 1000 rpm. The polymerization reaction was terminated by adding an excess of ethanol containing dilute hydrochloric acid, and the resulting copolymer of CO₂ and PO could be precipitated by adding more ethanol to the solution. To purify the precipitated copolymer, it was dissolved in THF first and then was reprecipitated by adding aqueous ethanol solution. After the purification, the copolymer collected was dried under vacuum at 50 °C for 40 h prior to analysis.

Analysis of the Copolymer. To determine the structure and the composition of the prepared copolymers, the NMR spectra of the copolymer in deuteriochloroform at room temperature were measured with a Burker AM-400 NMR spectrometer using tetramethylsilane as the standard, and the IR spectra were measured by a Perkin-Elmer 842 spectrometer. The molecular weights were determined with a Shimadzu C-R4A chromatopac by using THF as the solvent and polystyrene ($M_n = 4000$ to 6.5×10^5) as the standard.

Results and Discussion

Table 1 shows the results in copolymerization of CO₂ and PO by using several rare-earth-metal coordination catalysts in toluene at 60 °C and 400 psi. Each experiment was performed in duplicate; the difference in yield was observed to be less than 7.0%. From Table 1 it can be seen that only the catalyst system Y(CF₃CO₂)₃-Zn(Et)₂-glycerine could offer a high yield. It is also seen that the copolymerization could proceed for the catalyst system Zn(Et)₂-glycerine, though the yield was low, but not for the systems Y(CF₃CO₂)₃-glycerine and Y(CF₃CO₂)₃-Zn(Et)₂. This indicates that the active site might be on zinc in the compound formed by the reaction between Zn(Et)₂ and glycerine. A high yield resulting from the presence of Y(CF₃CO₂)₃ might be due to the fact that fluorine could induce a more positive charge of yttrium, or a bimetallic catalyst compound between Y(CF₃CO₂)₃ and the compound from the reaction between Zn(Et)₂ and glycerine could be formed. Further work is underway to identify the exact molecular structure and active site of this ternary catalyst system.

Table 2 shows the experimental results for different solvents. It is seen that less polar solvents, such as hexane and benzene, are not good candidates to make a polycarbonate from CO₂ and PO. While DMSO is the most polar solvent compared with the others, however, a yellowish copolymer rather than polycarbonate was obtained. This indicates that a proper choice of solvent is essential. When 1,3-dioxolane instead of toluene was used as the solvent, the yield and molecular weight of the resulting copolymer under the same operating conditions were found to improve significantly. The yield was increased from 3000 to 4200 (g/mol of Y)/h and M_n from 5.0×10^4 to 1.0×10^5 . As we were concerned with yield and molecular weight, further runs

Table 2. Effect of Solvent on Copolymerization of CO₂ and PO Using the Catalyst System Y(CF₃CO₂)₃-Zn(Et)₂-Glycerine^a

solvent	yield, (g/mol of Y)/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
toluene	3000	5.0	1.55	3.10
1,3-dioxolane	4200	10.0	2.85	2.85
n-hexane	trace			
benzene	680	5.1	1.68	3.29
DMSO	trace			

^a I = 0.00055 mol; II = 0.011 mol; III = 0.0055 mol; III/I = 20; III/II = 0.5; PO = 30 mL; solvent = 20 mL; T = 60 °C; P = 400 psi; time = 12 h.

Table 3. Effect of the Molar Ratio of II to I on Copolymerization of CO₂ and PO^a

molar ratio, II/I	yield, (g/mol of Y)/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
10	1900	6.0	2.40	4.00
15	2450	7.9	2.50	3.16
20	4200	10.0	2.85	2.85
25	2400	11.0	2.55	2.31
30	1840	11.5	2.79	2.42

^a II = 0.011 mol; III = 0.0055 mol; III/II = 0.5; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; T = 60 °C; P = 400 psi; time = 12 h.

Table 4. Effect of the Molar Ratio of III to II on Copolymerization of CO₂ and PO^a

molar ratio, III/II	yield, (g/mol of Y)/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
0.25	1000	3.0	1.06	3.52
0.375	2000	7.3	2.30	3.15
0.5	4200	10.0	2.85	2.85
0.625	1400	4.5	2.50	5.55
0.75	450	2.4	0.95	3.95

^a I = 0.0055 mol; II = 0.011 mol; III/I = 20; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; T = 60 °C; P = 400 psi; time = 12 h.

were focused on the use of Y(CF₃CO₂)₃-Zn(Et)₂-glycerine as catalyst and 1,3-dioxolane as solvent. Chen et al.¹⁵ pointed out that the component ratios in the Y(P₂₀₄)₃-Al(*i*-Bu)₃-glycerine system have a significant effect on yield in production of a random polycarbonate; the same conclusion can be drawn in production of an alternating polycarbonate using the present catalyst system. Table 3 shows that the optimum Zn(Et)₂/Y(CF₃CO₂)₃ molar ratio was 20 at which the yield and the molecular weight of the copolymer were highest though the dispersity was not at a maximum. The effect of the molar ratio of glycerine to Zn(Et)₂ is shown in Table 4. The most appropriate ratio providing the highest yield and M_w as well as the lowest dispersity was found to be at 0.5. The yield of 4200 (g/mol of Y)/h obtained in this study is much higher than that reported by Chen et al.¹⁵ (2451 g/mol of Y) for a 16 h run) despite the fact that the carbonate contents in these two copolymers are quite different.

The IR and NMR spectra of the resulting copolymer for the II/I molar ratio at 20 and the III/II molar ratio at 0.5, shown in Figures 1 and 2, indicate that the copolymer was indeed an alternating polycarbonate and the ratio of carbonate unit in total polymer calculated according to the reference² was 95.6%. Compared to the 10–30% of carbonate unit in a random polycarbonate as reported by Chen et al.,¹⁵ it is rational to speculate that the present catalyst system could more easily attract carbon dioxide to participate in copolymerization. Under this situation, the polypropylene oxide content in the resulting polycarbonate should be small. The

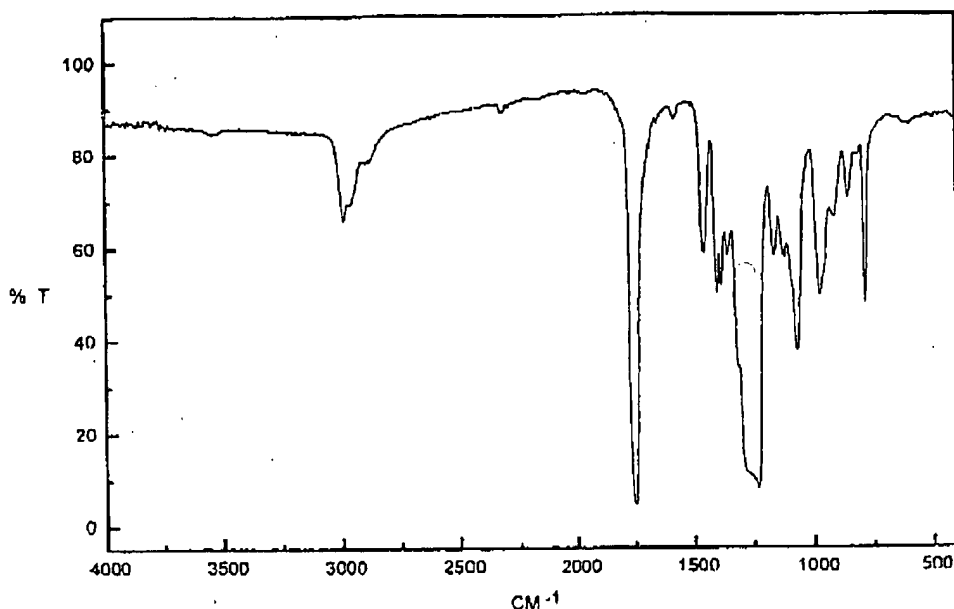


Figure 1. IR spectrum of the resulting copolymer. Reaction conditions: I = 0.00055 mol; II = 0.011 mol, III = 0.0055 mol; solvent = 1,3-dioxolane; PO = 30 mL; $T = 60^\circ\text{C}$; $P = 400$ psi; time = 12 h.

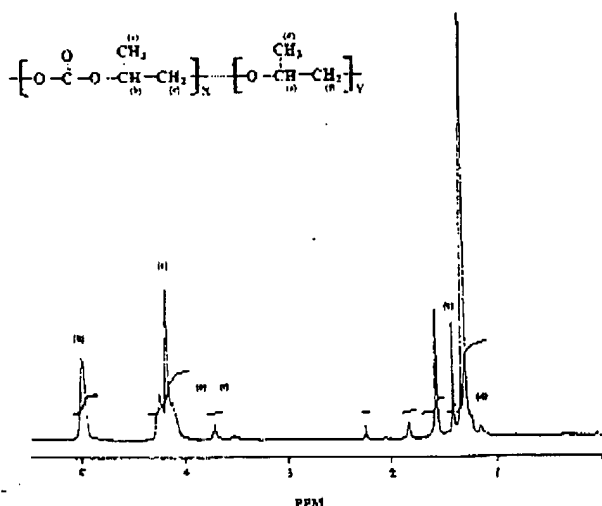


Figure 2. NMR spectrum of the resulting copolymer. Reaction condition: I = 0.00055 mol; II = 0.011 mol; III = 0.0055 mol; solvent = 1,3-dioxolane; PO = 30 mL; $T = 60^\circ\text{C}$; $P = 400$ psi; time = 12 h.

NMR spectrum in Figure 2 verifies this speculation. If the yield is based on the PO monomer used, a 63.5% yield in a 12 h run and a 72% yield in a 24 h run were observed for the proposed catalyst system with the most appropriate II/I and III/II molar ratios. Compared to the 88% content of carbonate unit in an alternating polycarbonate for the catalyst system $\text{Zn}(\text{Et})_2\text{-H}_2\text{O}^2$ and the 71.7% yield in a 44 h run for the catalyst system $\text{Zn}(\text{Et})_2\text{-}m\text{-hydroxybenzoic acid}$,¹¹ which is one of the best binary catalyst systems,³ the proposed ternary catalyst system seemed to be rather effective for generation of an alternating polycarbonate from CO₂ and PO.

When the molar ratios of II/I and III/II were maintained at 20 and 0.5, respectively, and the pressure was fixed at 400 psi, Table 5 shows that the yield increased with increasing temperature in a lower temperature range, reached a maximum at about 60°C , and then

Table 5. Effect of Temperature on Copolymerization of CO₂ and PO^a

$T, ^\circ\text{C}$	yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
40	470	3.2	1.60	5.00
50	995	5.1	2.55	4.90
60	4200	10.0	2.85	2.85
70	1600	3.5	1.60	4.57
80	1100	3.0	1.20	4.00
100	trace			

^a I = 0.00055 mol; II = 0.011 mol; III = 0.0055 mol; II/I = 20; III/II = 0.5; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; $P = 400$ psi; time = 12 h.

Table 6. Effect of Pressure on Copolymerization of CO₂ and PO^a

P, psi	yield, (g/(mol of Y))/h	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	M_w/M_n
200	3765	7.4	2.10	2.83
400	4200	10.0	2.85	2.85
600	4150	11.0	3.30	3.00
800	3350	8.0	2.90	3.62
1200	1890	7.9	3.30	4.17
1600	1390	7.0	2.66	3.80

^a I = 0.00055 mol; II = 0.011 mol; III = 0.0055 mol; II/I = 20; III/II = 0.5; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; $T = 60^\circ\text{C}$; time = 12 h.

dropped rapidly as the temperature further increased. The decrease of yield with increasing temperature is probably due to polymer degradation reactions. The location of the optimum temperature for production of an alternating polycarbonate is the same as that for production of a random polycarbonate.¹⁵

For a polymerization reaction, the difference in the partial molar volumes of the activated complex and the reactants is generally negative; consequently, the reaction rate is more often enhanced by pressure according to the transition state theory.^{4,17,18} For this copolymerization reaction, the yield was indeed enhanced with pressure as the pressure is less than 600 psi, but after that pressure was reached, the yield was decrease with increasing pressure, as shown in Table 6. One of the possible reasons is due to the swelling of the solvent

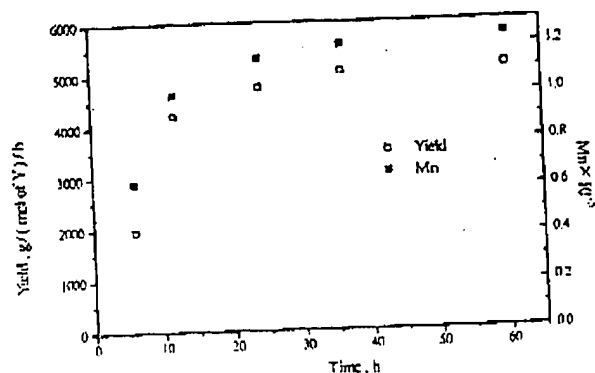


Figure 3. Reaction time dependence of the yield and molecular weight of the copolymer. Reaction conditions: I = 0.00055 mol; II = 0.011 mol; III = 0.0055 mol; solvent = 20 mL of 1,3-dioxolane; PO = 30 mL; $T = 60\text{ }^{\circ}\text{C}$; $P = 400\text{ psi}$.

because more CO_2 is dissolved in solvent at high pressures.^{19,20} As a result, the solubility of the copolymer is decreased. This explanation might be supported by the fact that the molecular weight of copolymer decreased with increasing pressure as $P > 600\text{ psi}$, shown in Table 6. Further studies are required to clarify the effects of pressure on yield and molecular weight.

Figure 3 illustrates the reaction time dependence of yield and molecular weight. Both the yield and molecular weight of the copolymer were found to increase with increasing reaction time. This indicates that the reaction mechanism for the copolymerization of CO_2 and PO is an anionic coordination process.¹⁰

Conclusion

An alternating polycarbonate was produced from the copolymerization of carbon dioxide and propylene oxide in the presence of the rare-earth-metal catalyst system $\text{Y}(\text{CF}_3\text{CO}_2)_3$ (I)—diethylzinc (II)—glycerine (III). The optimum yield and a high molecular weight of polycarbonate were obtained when the molar ratios of II/I and III/II were at 20 and 0.5, respectively, and the operating temperature and pressure were at $60\text{ }^{\circ}\text{C}$ and 400 psi, respectively, by using 1,3-dioxolane as solvent. The yield at those combined conditions in a 12 h run was 4200 (g/(mol of Y))/h. The carbonate content in the resulting copolymer was found to be 95.6%.

The use of CO_2 as a monomer to produce polycarbonate as investigated in this study may provide a means to consume CO_2 , which is a known contributor to global warming. Since the rare-earth-metal catalyst systems are so effective, more attention should be paid to apply this kind of catalyst system to other copolymerization reactions using CO_2 as the starting monomer.

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Copolymerization of Carbon Dioxide, Propylene Oxide, and Cyclohexene Oxide by a Yttrium-Metal Coordination Catalyst System

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INTRODUCTION

The copolymerization of CO₂ with epoxides to result in polycarbonate is one of the possible means for utilization of CO₂. But due to the fact that CO₂ is a relatively unreactive compound, an effective catalyst is required. For production of an alternating polycarbonate the organometallic catalyst systems consisting of dialkylzinc and a compound having two active hydrogens have been extensively studied (1-5). Using this kind of reaction systems, however, a long reaction time is usually required and yield needs to be improved. A ternary rare-earth-metal coordination system Y(P₂O₄)₃-Al(i-Bu)₃-glycerine was reported recently to carry out the copolymerization of CO₂ and PO (6). Despite that a random polycarbonate was produced, a higher molecular weight with a narrower molecular weight distribution and a higher yield within a shorter reaction period could be obtained compared to the binary organometallic catalyst systems. When the ternary rare-earth-metal coordination system containing Y(CF₃CO₂)₃, Zn(Et)₂, and glycerine was used to proceed the copolymerization of CO₂ and PO, an alternating polycarbonate with a carbonate content of 95.6% instead of a random polycarbonate could be generated (7). In addition to carbonate content, a much higher yield was observed using this reaction catalyst system.

Though a high molecular weight of polycarbonate can be generated by the copolymerization of CO₂ and PO, thermal stability of the resulting copolymer is relatively low, for example, T_g is about 308 K, and the temperature at which 10% weight loss occurs (T₁₀) is about 463 K. One possible means to improve thermal

stability is to add a third monomer with a different chemical structure in copolymerization. The objective of this paper is therefore to systematically study the copolymerization of CO₂, propylene oxide, and cyclohexene oxide catalyzed by a ternary yttrium-metal coordination catalyst system.

EXPERIMENTAL

Propylene oxide of a purity of 99.5% (Janssen Chimica) and cyclohexene oxide with a purity of 98% (Lancaster Synthesis) were treated by vacuum distillation before use. Diethylzinc, glycerine, and all the solvents, such as n-hexane, toluene, DMSO, 1,3-dioxolane, and THF, were of analytical reagent and used without further purification. CO₂ with a purity of 99.99% (Air Product) was used as received. Yttrium trifluoroacetate, yttrium acetate, yttrium 2-ethylhexanonate, yttrium acetylacetonate, and yttrium nitrate purchased from Aldrich Chemical Co. were heated in vacuum at 353 K for 40 h before use.

The catalyst system containing yttrium compound, Zn(Et)₂, and glycerine was prepared in an atmosphere of purified argon. Glycerine was added dropwise to a solution of Zn(Et)₂ in solvent at room temperature. After ethane gas evolution had ceased, the solution containing white powders resulting from the reaction between Zn(Et)₂ and glycerine was heated at 333 K for 2 h. This solution was then added to an autoclave which contained a known amount of yttrium compound. The resultant catalyst was stirred at 333 K for 1 h prior to CO₂, PO, and CHO being introduced.

Copolymerization of CO₂, PO, and CHO was carried out in a 300 ml autoclave which was equipped with a magnetic stirrer (Autoclave Engineers Inc.). The spinning speed was kept at 1000 rpm. After a certain pe-

Table 1.
Copolymerization of CO₂, PO, and CHO by Different Catalyst Systems*

catalyst system			yield, g/(mol of Y)/h	Mn × 10 ⁴	Mw × 10 ³	Mw/Mn
(I)	(II)	(III)				
Y(CF ₃ CO ₂) ₃	Zn(Et) ₂	Glycerine	7948	5.5	2.53	4.63
Y(CH ₃ CO ₂) ₃	Zn(Et) ₂	Glycerine	trace			
Y(CH ₃ COCH- C(O-CH ₃)) ₃	Zn(Et) ₂	Glycerine	5644	6.6	2.63	3.97
Y(CH ₃ (CH ₃) ₂ C H(C ₂ H ₅)CO ₂) ₃	Zn(Et) ₂	Glycerine	6069	7.0	3.52	3.59
Y(NO ₃) ₃	Zn(Et) ₂	Glycerine	6663	7.5	2.85	3.83

* I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; T = 353 K; P = 27.2 atm; time = 12 h

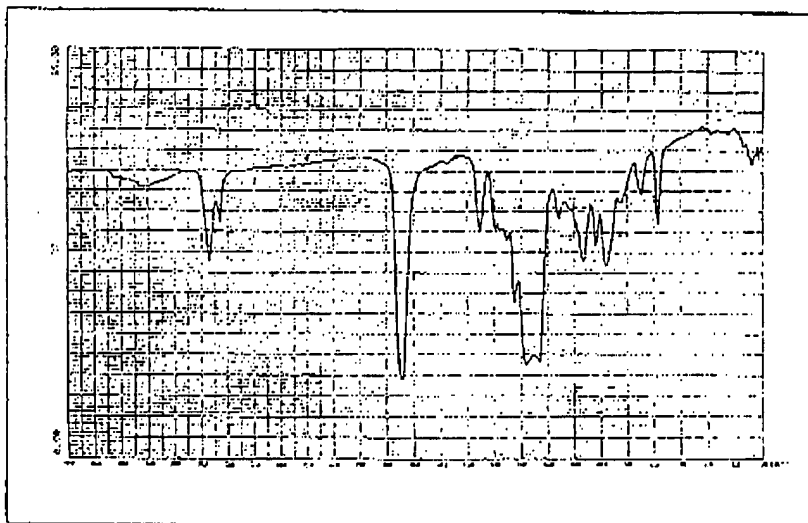
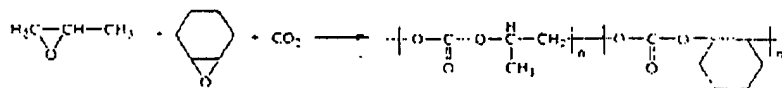


Figure 1. IR spectrum of the resulting copolymer.

riod of reaction time, the pressure in the autoclave was allowed to reduce to atmosphere. To collect the resulting copolymer in the autoclave, THF was introduced into the autoclave first to dissolve the copolymer and then the solution was added by an aqueous methanol solution to cause a precipitation. The copolymer reprecipitated was dried in vacuum at 303 K for 8 h before analysis.

To determine the structure and the composition of the copolymers generated, the ¹H and ¹³C NMR spectra were measured by a Bruker AM-300 NMR spectrometer and the IR spectra by a Jasco J-0085 spectrome-

ter. The molecular weights were determined by a gel permeation chromatography (Waters 150-CV). The



glass transition temperature and the T₁₀ were measured by a DSC (duPont 2900) and a TGA (duPont 951).

RESULTS AND DISCUSSION

In the beginning of the study, screening of solvents was first performed. The experimental results in-

dicated that a less polar solvent—n-hexane and a more polar solvent—DMSO were not good candidates to make polycarbonate from CO₂, PO, and CHO. Regarding yield and molecular weight distribution, 1,3-dioxolane was found to be superior to toluene. At least a 40% increase in yield and a narrower molecular weight distribution of the resulting copolymer using 1,3-dioxolane compared to toluene were observed. These results indicate that a proper choice of solvent is essential in copolymerization. Since 1,3-dioxolane showed its excellence, it was used as solvent in the following runs.

Table 1 shows the experimental results using different yttrium coordination catalyst systems in 1,3-dioxolane at 353 K and 27.2 atm. Each experiment was performed in duplicate, the difference in yield was observed less than 7.0%. It is seen from Table 1 that the catalyst system Y(CF₃CO₂)₃-Zn(Et)₂-glycerine provided the highest yield. It might be due to the fact that fluorine induced a more positive charge of yttrium, as a consequence, the coordination catalyst could adsorb CO₂ more easily.

The IR, ¹H- and ¹³C-NMR spectra of the resulting copolymer shown in Figures 1 to 3, respectively, indicate that the copolymer was an alternating polycarbonate and the copolymerization reaction took place according to the following scheme.

Since the polypropylene oxide and polycyclohexene oxide contents in the resulting copolymer were small, sorption rate of CO₂ on the present catalyst was believed to be fast.

When the molar ratios of II/I and III/II were maintained at 20 and 0.5, respectively, and the pressure was

fixed at 27.2 atm, Table 2 shows that the yield increased with increasing temperature in a lower temperature range, reached a maximum at about 353 K, and then dropped as the temperature further increased. The existence of an optimum temperature in the copolymerization of CO₂, PO, and CHO is also observed in the copolymerization of CO₂ and PO (7). According to the transition state theory (8), high-pressure operations are usually more favorable to polymerization reactions. For this copolymerization reaction, the yield was indeed enhanced with pressure as the pressure was less than 27.2 atm, but after that pressure was reached, the yield decreased with increasing pressure, shown in Table 3. One possible reason for the decrease in yield is due to the decrease in solubility of copolymer resulted from the swelling of the solvent caused by the dissolution of CO₂.

Tan and Hsu (7) pointed out that the component ratios in a rare-earth-metal coordination catalyst system have significant effects on yield and molecular weight in copolymerization of CO₂ and propylene oxide, the same conclusion can be drawn here. From the experimental results over wide ranges of the molar ratios of II to I and III to II, it was observed that the II/I and III/II ratios of 20 and 0.5, respectively, provided the highest yield though not the largest molecular weight and the best Mw/Mn.

It is seen from Table 4 that only one T_g was observed when the feed contained more CHO than PO. On the other hand, two glass transition temperatures existed. This observation might provide two aspects: 1) block copolymer could be produced by changing the monomer ratio in feed, 2) The ring-opening rate of PO is faster than that of CHO. In addition to generating a higher T_g polycarbonate, all the T_{10} of the present copolymers were found to increase at least 60 K compared to the copolymer resulting from CO₂ and PO.

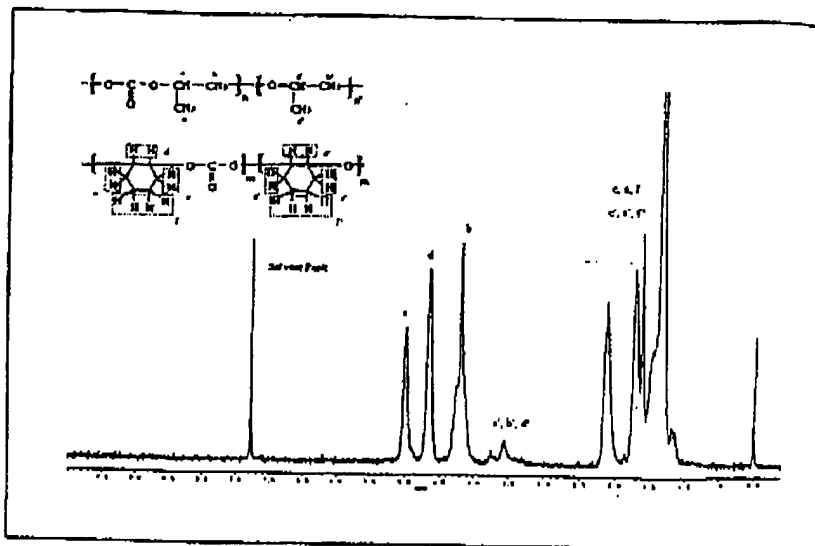


Figure 2. ¹H-NMR spectrum of the resulting copolymer.

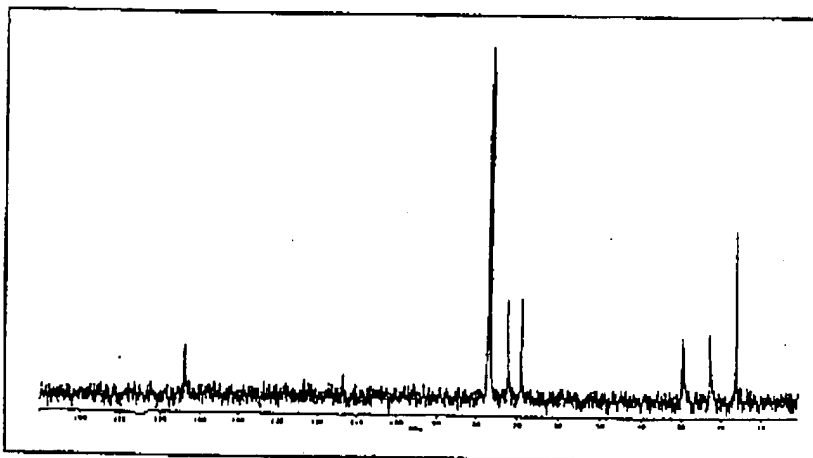


Figure 3. ¹³C-NMR spectrum of the resulting copolymer.

Table 2.
Effect of Temperature on Copolymerization of CO₂, PO, and CHO*

T, K	yield, g/(mol of Y) ² h	M _n × 10 ⁻³	M _w × 10 ⁻³	M _w /M _n
323	3475	7.4	5.02	6.94
333	6027	6.3	4.34	6.91
343	6792	6.0	3.78	6.33
353	7948	5.5	2.53	4.63
363	6046	4.2	2.46	5.88
373	5683	3.5	1.76	5.08

* I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; P = 27.2 atm; time = 12 h

Table 3.
Effect of Pressure on Copolymerization of CO₂, PO, and CHO*

P, atm	yield, g/(mol of Y)/h	Mn × 10 ⁻⁴	Mw × 10 ⁻⁴	Mw/Mn
20.4	6384	5.7	2.66	4.64
23.8	6717	6.0	3.81	6.34
27.2	7948	5.5	2.53	4.63
30.6	7710	5.3	2.95	5.58
34.0	7604	5.3	3.15	5.96
40.9	7210	5.9	3.29	5.55
47.6	7069	5.3	3.37	6.35

* I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; T = 353 K; time = 12 h

Table 4.
Effect of Monomer Ratio on Yield and Molecular Weight*

PO ml	CHO ml	yield		Mn × 10 ⁻⁴	Mw × 10 ⁻⁴	Mw/Mn	T _g , K	T _m , K
		g	%					
10	20	13.24	76.72	9.3	3.72	4.02	343	549
10	30	40.32	68.94	6.4	2.08	3.23	371	545
10	40	47.75	64.82	8.3	3.88	4.67	390	550
15	15	38.15	90.34	5.5	2.53	4.63	313,370	543
20	20	40.67	72.23	5.2	1.75	3.40	319,371	551
20	30	28.59	69.50	5.3	1.66	3.13	319,361	533
30	10	35.56	65.71	3.5	1.06	3.03	320,357	544
40	10	37.51	55.90	6.5	2.29	3.52	319,368	528
30	20	44.78	64.51	7.1	2.55	3.58	321,371	540

* I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; P = 27.2 atm; T = 353 K; time = 12 h

CONCLUSIONS

Polycarbonate could be produced effectively from the copolymerization of carbon dioxide, propylene oxide, and cyclohexene oxide in 1,3-dioxolane with a catalyst system consisting of Y(CF₃CO₂)₃, diethylzinc, and glycerine. At a proper combination of temperature, pressure, and molar ratios of the catalyst components, a very high yield up

to 7948 g/(mol of Y)/h and a molecular weight as high as 2.5×10^5 were observed in a 12 h run in a batch-mode operation.

A copolymer containing random distribution of PO carbonate and CHO carbonate or a block copolymer could be generated by varying the volume ratio of the monomers PO and CHO in feed. When the volume of CHO was greater than that of PO,

only one T_g of the resulting copolymer existed, otherwise, two glass transition temperatures existed. All the T_g of the present copolymer were found to be higher than that of the copolymer from CO₂ and PO. In addition, the T₁₀ was found to be higher. This indicates that the thermal properties of the resulting polycarbonate can be modified by introducing a third monomer with a different chemical structure.

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Polymer Communication

Block copolymerization of carbon dioxide with cyclohexene oxide and 4-vinyl-1-cyclohexene-1,2-epoxide in based poly(propylene carbonate) by yttrium–metal coordination catalyst

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Abstract

The coordination system, $Y(CF_3CO_2)_3$ (I)– $Zn(Et)_2$ (II)–*m*-hydroxybenzoic acid (III), was found to be the most active catalyst to generate poly(propylene carbonate) (PPC) from carbon dioxide and propylene oxide (PO) in 1,3-dioxolane. A high yield and a high molecular weight could be obtained at the conditions of a I/II molar ratio of 20, a II/III molar ratio of 1.0, a temperature of 60 °C, and a pressure of 2.76 MPa. The carbonate content in the resultant PPC was found to be nearly 100%.

The block copolymerization in the based PPC was carried out by *in situ* introducing an epoxide other than PO right after the copolymerization of carbon dioxide with PO using the same catalyst system. The IR and 1H NMR spectra as well as the measured molecular weights verified the resulting copolymers were block copolymers. For the block copolymerization of CO_2 with cyclohexene oxide and CO_2 with 4-vinyl-1-cyclohexene-1,2-epoxide in the based PPC, the yield as well as the cyclohexene carbonate and the 4-vinyl-1-cyclohexene carbonate contents were found to increase with increasing temperature. The most appropriate temperature was around at 80 °C. The weight-average molecular weights of the block copolymers lay in a range from 2.44×10^5 to 3.16×10^5 , the polydispersity in a range from 5.0 to 6.3, and the 10% weight loss temperature in a range from 226 to 253 °C. The thermal and mechanical properties of the resultant block copolymers lay between those of PPC, poly(cyclohexene carbonate), and poly(4-vinyl-1-cyclohexene carbonate), indicating the desired properties of a polymer can be achieved via block copolymerization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon dioxide; Epoxide; Polyetherscarbonate

1. Introduction

Carbon dioxide is a major greenhouse gas. Its emission into atmosphere is therefore needed to reduce. One of the means to consume CO_2 is to use it as the starting monomer to synthesize polycarbonate. This means also meets the concept of the cleaner production, because toxic monomers such as phosgene are not environmentally acceptable in preparation of polycarbonate. Due to the inert characteristics of CO_2 , an effective catalyst is generally required to proceed this kind of polymerization. The polymerization of CO_2 with propylene oxide (PO) was first reported in 1969 [1]. An alternating poly(propylene carbonate) (PPC) with a carbonate content of 88% was synthesized using diethyl zinc/water as the catalyst. After that, many

other catalyst systems including: (a) zinc-based catalyst, such as $Zn(C_2H_5)_2 \cdot H_2O$, $Zn(C_2H_5)_2$ -di- or tri-hydric phenol, and multiprotic compounds [2–5]; (b) $(tpp)AlCl$ and its derivatives [6]; (c) zinc salts [7] were appeared in the literature for the copolymerization of CO_2 and PO. Due to low yield and long reaction time, many attempts to improve catalyst activity have been made. For the zinc-based catalysts, the use of diethyl zinc/polyhydric phenol [8], zinc glutarate and its derivatives [9,10], and cadmium(II) carboxylates [11] as the catalysts was found to indeed improve the reactivity of CO_2 with PO. For the $(tpp)AlCl$ catalyst systems, the reactivity could also be enhanced using aluminum porphyrin and diethylaluminum chloride-25,27-di-methoxy-26,28-dihydroxy-*p*-*tert*-butyl-calix-4-arene [12,13] as the catalysts.

In recent publications, rare earth coordination catalysts exhibited its high activity in the ring-opening polymerization of epoxides and episulfides [14–18].

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Table 1

Effect of rare-earth compound (I) on the copolymerization of CO₂ with PO (I = 0.0004 mol; II = 0.008 mol; III = 0.008 mol; solvent = 30 ml of 1,3-dioxolane; PO = 30 ml; T = 60 °C; P = 2.76 MPa; time = 12 h)

Catalyst system			Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}
I	II	III				
Y(CF ₃ CO ₂) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	50	13.5	4.7	100
Ce(acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	9	8	5.3	96
La(acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	29	12.2	3.9	96
Nd(acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	23	5.6	2.9	96
Sm(acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	8	7.1	3.9	93
Y(acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	23	7.5	3.3	91
Ce(trifluoro-acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	27	8.3	4.2	94
Nd(trifluoro-acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	31	13.3	4.4	96
Sm(trifluoro-acac) ₃	Zn(Et) ₂	<i>m</i> -Hydroxybenzoic acid	12	3.0	2.1	93

was carried out in the autoclave containing the prepared catalyst system at a spinning speed of 1000 rpm. After a certain period of reaction time, the pressure was reduced to atmosphere to terminate the copolymerization and an excess of aqueous methanol solution containing dilute hydrochloric acid was added to result in a precipitation of the copolymer. To purify the precipitated crude copolymer, it was dissolved in THF first and then was precipitated again by adding an aqueous methanol solution. After three-time purification treatment, the resultant copolymer was dried under vacuum at 50 °C for 40 h prior to analysis.

2.3. Block copolymerization

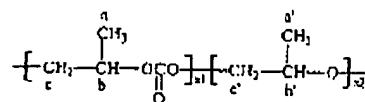
The block copolymerization was carried out by in situ introducing the epoxide other than PO into the autoclave at a time when the based PPC had been synthesized via the copolymerization of carbon dioxide and PO. After a certain period, the pressure in the autoclave was reduced to atmosphere to terminate the block copolymerization. The resulting block copolymer was obtained and purified by the same procedures as mentioned for the synthesis of PPC.

2.4. Analysis of the copolymer

The structure and the composition of the resulting copolymers were determined by the IR and ¹H NMR spectra. The IR spectra were obtained by a Perkin-Elmer 842 spectrometer and the ¹H NMR spectra of the copolymer in *n*-chloroform at room temperature using tetramethylsilane as the internal reference were obtained by a Varian Unitynova 500 NMR spectrometer.

2.4.1. PPC synthesized from CO₂ and PO

Suppose the resultant PPC possessed the following structure:



Three major peaks should be present in the ¹H NMR spectrum. One was attributed from CH in carbonate unit (b: δ = 5.0), the other from CH₂ in carbonate unit (c: δ = 4.1–4.25), and the third one from CH and CH₂ in ether unit

Table 2

Effect of multiprotic compound (III) on the copolymerization of CO₂ with PO (I = 0.0004 mol of Y(CF₃CO₂)₃; II = 0.008 mol of Zn(Et)₂; solvent = 30 ml of 1,3-dioxolane; PO = 30 ml; T = 60 °C; P = 2.76 MPa; time = 12 h)

Multiprotic compound	Molar ratio, III/II	Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}
1,2,3-Benzenetricarboxylic acid	0.5	—	—	—	—
1,2,3-Benzenetricarboxylic acid	0.34	6	6.8	3.4	100
Glycerine	0.5	28	6.4	3.4	100
Glucose	0.5	—	—	—	—
Glucose	0.375	—	—	—	—
Glucose	0.25	—	—	—	—
<i>m</i> -Hydroxybenzoic acid	0.75	19	8.2	4.3	100
<i>m</i> -Hydroxybenzoic acid	1	50	13.5	4.7	100
<i>m</i> -Hydroxybenzoic acid	1.25	39	11.6	4.8	100
1,3-Phenylene diamine	0.625	32	13.4	5.4	94
1,3-Phenylene diamine	0.5	38	14.0	5.2	98
1,3-Phenylene diamine	0.375	30	12.3	5.3	92
Pyrogallol	0.5	45	7.9	3.4	100
Resorcinol	1	49	11.1	4.6	100

Table 3

Effect of solvent on the copolymerization of CO₂ with PQ by the catalyst system Y(CF₃CO₂)₃-Zn(Et)₂-*m*-hydroxybenzoic acid (I = 0.0004 mol of Y(CF₃CO₂)₃; II = 0.008 mol of Zn(Et)₂; III = 0.008 mol of *m*-hydroxybenzoic acid; PQ = 30 ml; T = 80 °C; P = 2.76 MPa; time = 12 h)

Solvent	Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}
1,3-Dioxolane (30 ml)	30	13.5	4.7	100
EA (3 ml) + 1,3-dioxolane (27 ml)	39	8.6	3.7	96
EA (7.5 ml) + 1,3-dioxolane (22.5 ml)	35	6.0	3.2	100
EA (15 ml) + 1,3-dioxolane (15 ml)	22	4.9	2.5	98
Acetone (30 ml)	—	—	—	—
THF (30 ml)	20	11.5	2.9	97
Acetone (15 ml) + THF (15 ml)	—	—	—	—
Acetone (15 ml) + 1,3-dioxolane (15 ml)	—	—	—	—

copolymerization of CO₂ and PQ using different rare-earth compounds in the solvent of 1,3-dioxolane at 60 °C and 2.76 MPa. Each experiment was performed in duplicate. The differences in yield, M_w , M_n , and T_{10} were found to be always less than 6.0%, indicating that the data could be reproduced. From Table 1, it is seen that the rare-earth metal trifluoroacetate and trifluoroacetylacetonates were more active than the rare-earth-metal acetylacetonates for this copolymerization. This might be due to the presence of fluorine induced a more positive charge of the rare-earth metal. In a consequence the positive charge of zinc was also increased due to the presence of the bond rare-earth metal-O-Zn formed in the catalyst preparation step. In the comparison of the rare-earth metal coordination systems, it can be seen that the system Y(CF₃CO₂)₃-Zn(Et)₂-*m*-hydroxybenzoic acid provided the highest activity, molecular weight, and f_{CO_2} , though the polydispersity (M_w/M_n) was not the best.

When Y(CF₃CO₂)₃ was used as the rare-earth metal compound in the catalyst system, several multiprotic compounds and different ratios of III/II were tested to see their effects on yield and molecular weight of the resultant copolymers. Table 2 shows that the use of *m*-hydroxybenzoic acid with a molar ratio of *m*-hydroxybenzoic acid to Zn(Et)₂ as 1.0 resulted in the highest yield and molecular weight compared to other multiprotic compounds. Besides, the yield was found to be much higher than that using glycerine reported by Tan and Hsu [17]. A possible reason was that more positive charge of zinc was generated by *m*-hydroxybenzoic acid compared to glycerine because *m*-hydroxybenzoic acid is a more acidic compound. It is surprised to see from Table 2 that glucose could not proceed the copolymerization at all even it possesses six -OH bonds. It is known that a compound possessing more active hydrogen was beneficial for the copolymerization when organometallic catalyst consisting of diethylzinc was employed [4,19,22–24]. While polyethercarbonate could be generated using a tetraprotic compound 1,3-phenylene diamine, the yield and molecular weight were not comparable to *m*-hydroxybenzoic acid. Though pyrogallol could generate a high f_{CO_2} and a narrow polydispersity, the

molecular weight was found to be less than 80 000. A very low yield was observed when 1,2,3-benzenecarboxylic acid was used. The reason was that this compound became an acid anhydride after the removal of the crystalline water from its structure by heating before it was used. In a comparison of the acidity of the multiprotic compounds, it can be seen that the acidity increases in the following order: glycerine, pyrogallol, resorcinol, *m*-hydroxybenzoic acid. The present results indicated that a multiprotic compound with a high acidity was essential to yield a large amount of PPC.

Table 3 shows that solvent not only affected the catalyst activity but also the properties of the resultant copolymers. When a mixture of EA and 1,3-dioxolane was used as the solvent, it is seen that the catalyst activity decreased but the polydispersity became narrower when the EA content was increased. This was because that EA was a poor solvent for the resulting copolymer. The addition of EA therefore reduced the solubility of the resultant copolymer in the mixture. Under this circumstance, the molecular weight could not become very large and the polydispersity of the resultant copolymer therefore became narrower. On the other hand, acetone is a very good solvent for PPC; however, no PPC was generated when acetone was used either as the solvent or as the cosolvent. It seems that the copolymerization cannot be carried out in a very polar solvent. Regarding yield and molecular weight, Table 3 shows 1,3-dioxolane was the most appropriate solvent for this copolymerization compared to the other solvents and mixtures. It was therefore chosen for the subsequent block copolymerization.

The IR and ¹H NMR spectra of the resulting copolymer for the II/I molar ratio of 20 and the III/II molar ratio of 1.0 are shown in Figs. 1 and 2, respectively. The two adsorption peaks at 1250 and 1750 cm⁻¹ in Fig. 1 provided an evidence for the presence of carbonate unit in the resultant copolymer. The carbonate content could be evaluated from Fig. 2 with Eq. (1), and was found to be nearly of 100%. It should be mentioned that due to the peak areas at $\delta = 3.5$ –3.8 were nearly 0, the contribution to the carbonate content by the structures other than the previously

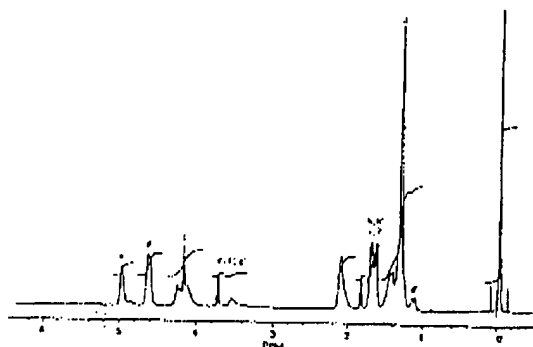


Fig. 5. The ^1H NMR spectrum of the block copolymer synthesized from CO_2 and CHO in the based poly(propylene carbonate). (Reaction conditions: CHO = 30 ml; $T = 80^\circ\text{C}$; $P = 4.14\text{ MPa}$; time = 12 h.)

the copolymerization of CO_2 with PO and CO_2 with CHO when the temperature was higher than 60 and 80°C , respectively. The block copolymerization was therefore carried out between 60 and 80°C in this study. Table 4 shows the yield and properties of the resulting PPC-block-PCHC at 60, 70, and 80°C . It can be seen that both the yield and weight-average molecular weight increased with temperature and the best polydispersity occurred at 70°C . The carbonate content lying between 86 and 92% at these temperatures indicated the presence of PO unit and CHO unit in the resultant block copolymer. It was also observed that the ratios of carbon and hydrogen atoms evaluated by the ^1H NMR spectrum and the elemental analysis were 53.0:6.9 and 53.4:7.0, respectively. The small differences in carbon and hydrogen atoms between these two calculation means indicated the calculated carbonate content be reliable. Table 4 shows more PO and CHO units were present at 80°C . As indicated by Hsu and Tan [18], the most appropriate temperature for the copolymerization of CO_2 with CHO occurred at 80°C . The copolymerization of CO_2 with CHO was thus accelerated with increasing temperature. As a result, F_{CHC} increased with increasing temperature. On the other hand, the degradation of the based PPC became more severe at the temperatures higher than 60°C . F_{PC} thus decreased with increasing temperature. Due to an increase in weight-average molecular weight with temperature as shown in Table 4, the copolymerization rate of CO_2 with CHO was believed to be higher than the degradation

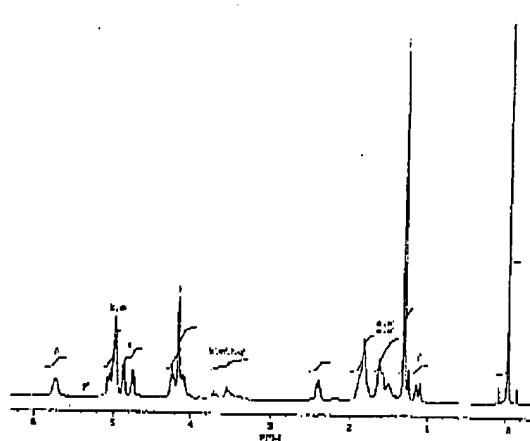


Fig. 6. The ^1H NMR spectrum of the block copolymer synthesized from CO_2 and VCHO in the based PPC. (Reaction conditions: VCHO = 30 ml; $T = 80^\circ\text{C}$; $P = 4.14\text{ MPa}$; time = 12 h.)

rate of PPC at 80°C . Table 5 shows similar results for the synthesis of PPC-block-PVCHC. A high carbonate content lying between 89 and 92% was present in the resultant block copolymer and F_{VCHC} increased with increasing temperature. Due to the copolymerization rate of PVCHC was lower than that of PCHC in the present temperature range [25], F_{VCHC} in this block copolymerization was found to be lower than F_{CHC} in the block copolymerization of CO_2 with CHO at these temperatures.

The glass transition temperatures (T_g) of the resultant copolymers and block copolymers based on PPC are shown in Table 6. It is seen that the resultant PPC-block-PCHC and PPC-block-PVCHC possessed two T_g that lay between those of the copolymers and were not equal to those of the polyethers, indicating that block copolymerization could be carried out using the present technique. Table 4 shows the T_{10} of PPC-block-PCHC were in a range $236\text{--}253^\circ\text{C}$ that was higher than that of the PPC (about 195°C) but lower than that of PCHC (about 280°C). It was also the case for the PPC-block-PVCHC, as shown in Table 5. These results indicated that the thermal property of the block copolymer could be varied by addition of a proper portion of the copolymer resulted from the copolymerization of CO_2 with CHO or VCHO.

Table 7 shows the mechanical properties of the resultant

Table 4

Experimental results for the block copolymerization of CO_2 with CHO in the based PPC at different temperatures (I = 0.0004 mol of $\text{Y}(\text{CF}_3\text{CO}_2)_3$; II = 0.008 mol of $\text{Zn}(\text{Et})_2$; III = 0.008 mol of *m*-hydroxybenzoic acid; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; $P = 4.14\text{ MPa}$; time = 12 h)

$T(^{\circ}\text{C})$	Yield, g/g of Zn	$M_w \times 10^{-4}$	M_w/M_n	f_{CO_2}	F_{PC}	F_{CHC}	$F_{\text{PC}} + F_{\text{CHC}}$	$T_{10}(^{\circ}\text{C})$
60	48	24.4	6.1	91	72	19	9	236
70	59	27.7	5.0	92	65	27	8	253
80	69	31.0	6.2	86	47	39	14	248

not conducting was found, when the structure of the matrix molecules, PEO and PEO sulfonic acid anion only is conceived. To study further the reason to the conductivity of cell4, instantaneous coordinations of the cations were studied. The main differences between the instantaneous coordination in non-conducting cell2 and in conducting cell4 are the coordination between cations and water and the coordination between cations and ether oxygen atoms. The coordination numbers between cations and end groups of the anions are much higher in cell4 than in cell2. The coordination between the ether oxygen atoms in PEO and the cations or between the ether oxygen atoms in the anion and the cations is much stronger in cell2 than in cell4. The water molecules are more coordinated to ether oxygen in cell2 than in cell4. In actual fact, a small microphase separation is found in cell4, where the water molecules are more coordinated to each other and to the end groups of the anions and less to the PEO chain than in cell4 than in cell2. This small microphase separation can promote the conductivity in cell4 compared to cell2.

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Synthesis of polyethercarbonate from carbon dioxide and cyclohexene oxide by yttrium–metal coordination catalyst

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Abstract

The copolymerization of carbon dioxide and cyclohexene oxide to generate polyethercarbonate using yttrium–metal coordination catalyst was carried out in this study. After testing several catalyst systems, it was found that the system consisting of $Y(CF_3CO_2)_3(III)$, $Zn(Et)_2(II)$, and glycerine(III) in the solvent of 1,3-dioxolane was the most effective catalyst. The IR and 1H NMR spectra indicated that the resulting copolymer was indeed a polyethercarbonate with a carbonate content as high as 100%. The weight-average molecular weights observed in a range between 1.9×10^4 and 3.3×10^5 and the dispersity between 3.5 and 12.5. The glass transition temperature of the resulting copolymer was found to locate in a range 105–128°C and the temperature at which 10% weight loss occurred in a range 252–331°C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon dioxide; Cyclohexene oxide; Yttrium compound

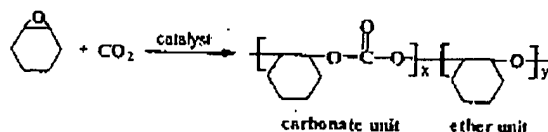
1. Introduction

Carbon dioxide is readily available, inexpensive, nontoxic, and need to be utilized to reduce its emission into atmosphere from global warming point of view, it can be considered as a starting monomer to substitute toxic monomers for synthesis of polymers [1,2]. Due to its inert and relatively unreactive characteristic, a catalyst is generally required to proceed these kind of reactions. Regarding the polymerization of carbon dioxide with epoxide, the first article appeared in 1969 in which an alternating poly(propylene carbonate) was synthesized from carbon dioxide and propylene oxide (PO) using diethyl zinc/water as catalyst [3]. Because of a long reaction time required for a low yield, many attempts to improve activity of catalyst for this copolymerization have been reported in the open literature [4–10]. The most commonly used catalyst systems consist of diethylzinc and a compound having two active hydrogen atoms, such as water, primary amines, carboxylic acids, etc.

Recently, rare-earth metal coordination catalysts were also used to synthesize polyethercarbonate from carbon dioxide and PO [11,12]. While a high molecular weight and a high carbonate content of poly(propylene oxide)

could be generated, its application has some limitations due to a low thermal stability. The glass transition temperature T_g of the resulting poly(propylene oxide) is about 35°C, and the temperature at which 10% weight loss occurred (T_{10}) is about 190°C.

To improve thermal stability, cyclohexene oxide (CHO), possessing a rigid six-membered ring, may be used to substitute PO as the starting monomer to synthesize a polyethercarbonate. The copolymerization of carbon dioxide and CHO was carried out according to the scheme



Zinc-based catalysts are generally used in this copolymerization reaction including zinc/water [13], zinc bisphosphonate(base)₂ [14–16], zinc crotonate [17], and fluorinated zinc compound [18,19]. In addition to zinc-based catalyst, chromium porphyrinate [20] was also used as the catalyst. As for the copolymerization of CO₂ and PO, a long reaction time is generally required to achieve a desired yield and a high molecular weight is sometimes difficult to obtain. Besides, the thermal properties of the resulting polyethercarbonate were not provided.

Since a rare-earth metal coordination catalyst exhibits its

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Table 2

Effect of solvent on copolymerization of CO₂ and CHO using the catalyst system Y(CF₃CO₂)₃–Zn(Et)₂–glycerine (I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 30 ml; CHO = 30 ml; T = 80°C; P = 400 psi; time = 12 h)

Solvent	Polarity index	Yield g of polymer/g of Zn	Mn × 10 ⁻⁴	Mw × 10 ⁻³	Mw/Mn	T _g (°C)	T ₁₀ (°C)	f _{CO₂}
n-Hexane	0.1	3	1.14	0.45	3.6	124	283	71.5
Toluene	2.4	62	1.33	1.38	10.4	117	252	62.4
Benzene	2.7	59	1.98	1.87	9.4	122	288	76.1
1,2-Dichloroethane	3.5	57	2.30	2.13	8.5	120	251	60.9
THF	4.0	70	2.07	1.14	5.5	122	253	95.6
Chloroform	4.1	54	2.66	2.61	9.8	119	283	100
Ethyl acetate	4.4	39	1.25	0.44	3.5	118	281	92.5
1,4-Dioxane	4.8	62	2.80	2.20	7.9	116	283	93.9
1,3-Dioxolane	5.3	63	3.34	2.48	7.4	123	272	100
DMF	6.4	Trace	–	–	–	–	–	–

resultant copolymers (f_{CO₂}) could be evaluated based on the following equation [19]:

$$f_{\text{CO}_2} = \frac{A_{4.8}}{A_{4.8} + A_{3.5}}$$

The molecular weights of the copolymers were determined by a gel permeation chromatograph (Shimadzu LC-9A) using polystyrene (Mn varies from 2698 to 650,000) as the standard. THF was used as the solvent with a flow rate of 1.0 ml min⁻¹ at 35°C. The glass transition temperature (T_g) and the temperature at which a 10 wt% loss occurs (T₁₀) were measured by a DSC (DuPont 2900) and a TGA (DuPont 951), respectively.

3. Results and discussion

Table 1 shows the experimental results in the copolymerization of CO₂ and CHO by using different yttrium–metal coordination catalysts in 1,3-dioxolane at 80°C and 400 psi. Each experiment was performed in duplicate, the differences in yield, Mw, and T_g were found to be always less than 6.0%. Under this situation, it is concluded that the data on this polymerization reaction could be reproduced. From Table 1, it is seen that the catalyst system Y(CF₃CO₂)₃–Zn(Et)₂–glycerine provided the highest activity and the highest f_{CO₂}. While polymerization could be proceeded using the catalyst system containing only Y(CF₃CO₂)₃ and

Zn(Et)₂, the resultant polymer had a very low f_{CO₂}, indicating that the main reaction was a homopolymerization of cyclohexene oxide rather than a copolymerization. But when the catalyst system consisted of only Y(CF₃CO₂)₃ and glycerine, neither poly(cyclohexene oxide) nor polyethercarbonate was found to form. On the other hand a polyethercarbonate could be produced by the catalyst system consisting of Zn(Et)₂ and glycerine, though the yield was lower than that by the system containing Y(CF₃CO₂)₃, Zn(Et)₂, and glycerine. All these results indicated that the active site was on zinc in a compound resulted from either by the reaction between Zn(Et)₂ and glycerine or between Y(CF₃CO₂)₃ and the compound formed from Zn(Et)₂ and glycerine.

Table 1 shows an yttrium compound containing fluorine which was superior to other yttrium compounds for this copolymerization reaction. This is because that the presence of fluorine could induce a more positive charge of yttrium. In a consequence the positive charge of zinc is also increased due to the presence of the bond Y–O–Zn formed by the reaction between the yttrium compound and the compound resulted from Zn(Et)₂ and glycerine. Under this situation carbon dioxide could be more easily attracted by the active sites, as a result a high yield and high carbonate content in the copolymer were obtained. Based on yield and f_{CO₂}, the system Y(CF₃CO₂)₃–Zn(Et)₂–glycerine was selected as the most appropriate catalyst system to carry out the copolymerization of CO₂ and CHO.

Table 3

Effect of the molar ratio of III to II on copolymerization of CO₂ and CHO (I = 0.0004 mol; II = 0.008 mol; solvent = 30 ml of 1,3-dioxolane; CHO = 30 ml; T = 80°C; P = 400 psi; time = 12 h)

Molar ratio, III/II	Yield g of polymer/g of Zn	Mn × 10 ⁻⁴	Mw × 10 ⁻³	Mw/Mn	T _g (°C)	T ₁₀ (°C)	f _{CO₂}
0	25	0.51	0.19	3.7	117	331	2.4
0.125	27	0.71	0.32	4.5	115	322	12.3
0.250	55	1.61	1.41	8.8	122	291	51.3
0.375	61	1.78	2.07	11.6	119	292	61.3
0.500	63	3.34	2.48	7.4	123	280	100
0.625	67	2.49	2.70	10.8	122	291	100
0.750	59	2.11	1.79	8.5	122	266	100
0.875	32	1.65	1.59	9.6	120	260	100

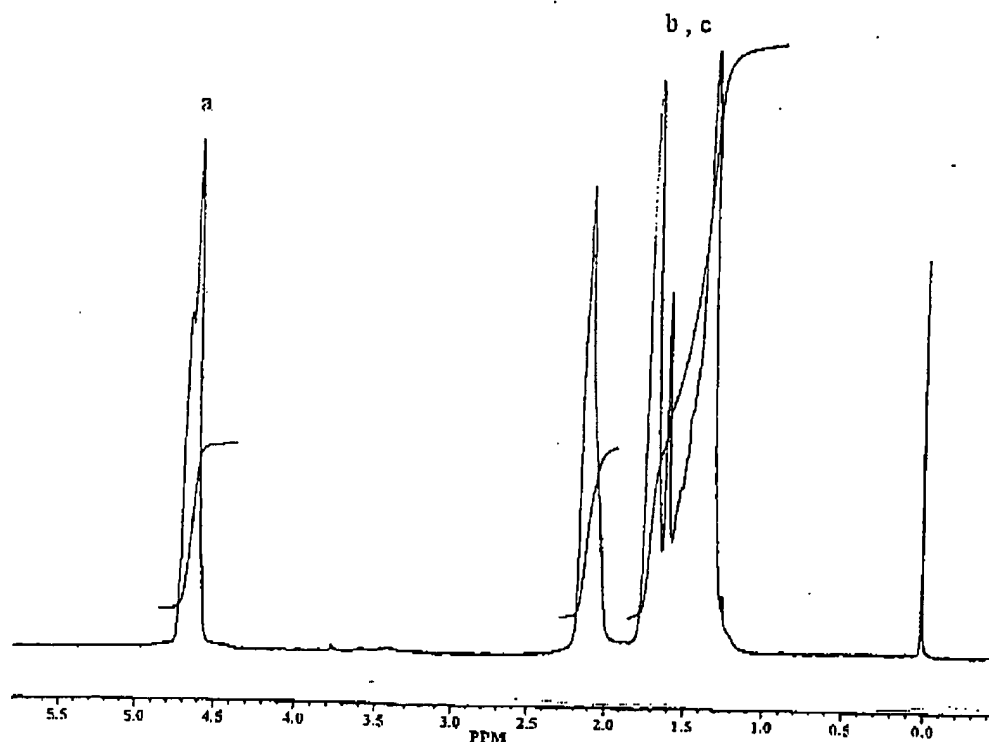


Fig. 2. ^1H NMR spectra of the resulting copolymer. Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 1,3-dioxolane; CHO = 30 ml; $T = 80^\circ\text{C}$; $P = 400$ psi; time = 12 h.

less than the stoichiometric requirement was used, the complex formed which would react further with $\text{Y}(\text{CF}_3\text{CO}_2)_3$ to generate active sites for the copolymerization of CO_2 and CHO became less. As a result a significant

portion of ether unit in the resulting copolymer, i.e. f_{CO_2} is less than 1.0, was observed. On the other hand, when more glycerine was used, it would hinder the attraction of CO_2 and CHO by the active sites in the coordination catalyst, the

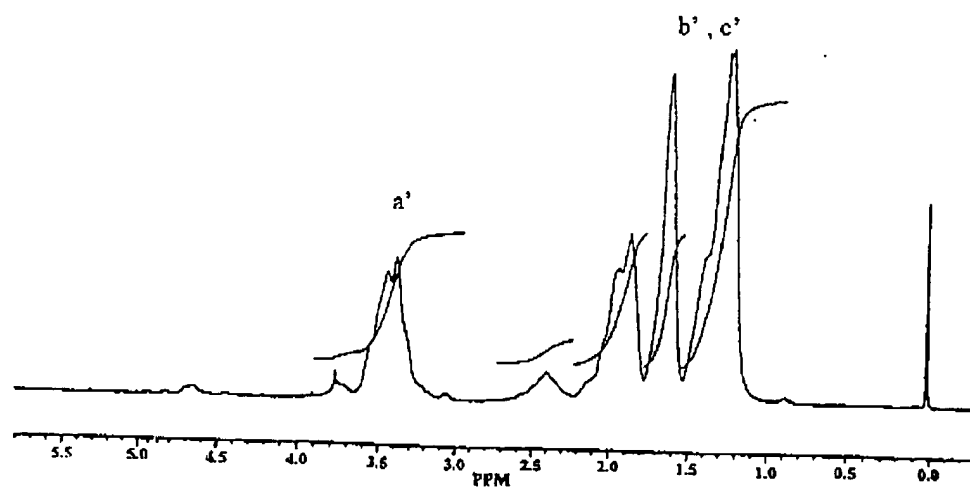


Fig. 3. ^1H NMR spectra of the resulting copolymer. Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0 mol; solvent = 1,3-dioxolane; CHO = 30 ml; $T = 80^\circ\text{C}$; $P = 400$ psi; time = 12 h.

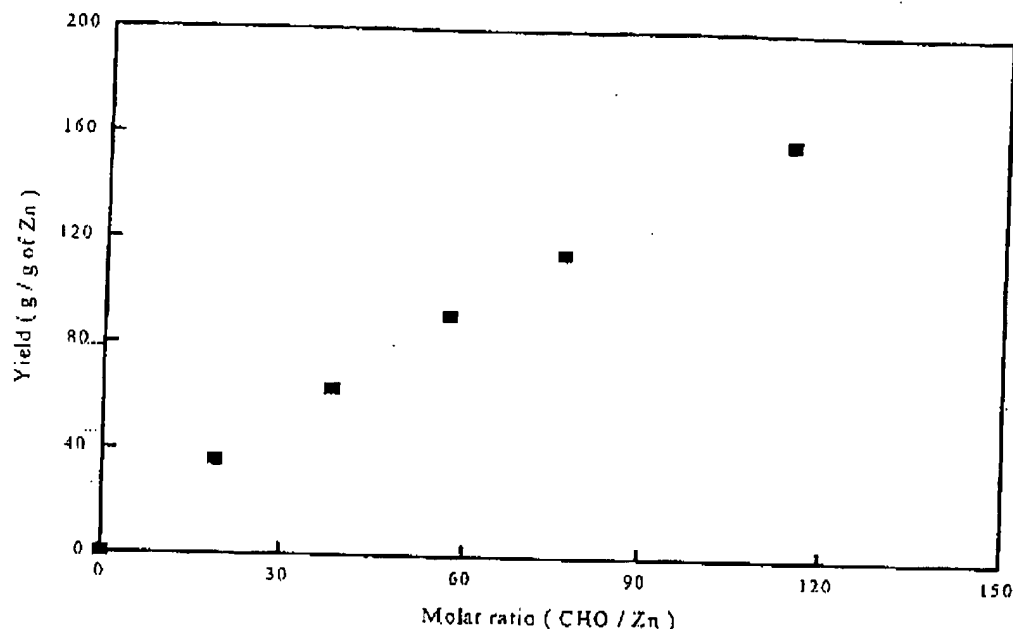


Fig. 4. The effect of the molar ratio of CHO to $\text{Zn}(\text{Et})_2$ on yield. Reaction conditions: I = 0.0004 mol; II = 0.008 mol; III = 0.004 mol; solvent = 1,3-dioxolane; $T = 80^\circ\text{C}$; $P = 400$ psi; time = 12 h.

ratio. These results indicate that sorption of CHO by the catalyst was crucial for this copolymerization. Due to volume limitation of the reactor, the molar ratio higher than 120 for an initial charge of $\text{Zn}(\text{Et})_2$ of 0.008 mol could not be obtained. In order to see this effect at higher molar ratios, 0.004 mol of $\text{Zn}(\text{Et})_2$ was charged initially into the reactor. When the molar ratio of CHO to $\text{Zn}(\text{Et})_2$ was at 300, the yield was observed to be 310.4 g/(g of Zn). This result is higher than or comparable to those reported in the literature [14,16,18,19]. It should also be noted that the operation time to achieve this high yield using the present catalyst system is less than those in the above-mentioned literature. In addition, the recovery of catalyst is relatively easy for the present catalyst due to its heterogeneity as compared to the homogenous catalyst reported.

It can be seen from Tables 1–6 that the glass transition temperature T_g of the resulting copolymer at any operating condition is higher than 105°C , which is significant larger than that of the copolymer generated from CO_2 and PO (about 35°C). In addition to T_g , T_{10} of the resultant polyethercarbonate was found to be higher than 252°C at any reaction condition exhibiting at least 60°C higher than that of the copolymer resulted from CO_2 and PO. These results indicated the copolymerization of CO_2 and CHO be a feasible means to generate a polyethercarbonate with a high T_g . The enhancement of thermal property for the present copolymer was attributed to the presence of a bulky group in CHO.

4. Conclusions

The polyethercarbonate could be generated from the copolymerization of carbon dioxide and cyclohexene oxide in 1,3-dioxolane by a catalyst system consisting of $\text{Y}(\text{CF}_3\text{CO}_2)_3$, diethylzinc, and glycerine. For this catalyst system, sorption of carbon dioxide onto active sites is believed to be fast, thus an alternating instead of a random polyethercarbonate could be obtained. With a proper combination of temperature, pressure, and molar ratio of the catalyst components for a 12 h run in a batch-mode operation a yield higher than 310.4 g/(g of Zn) could be obtained, indicating that this copolymerization is an effective means to utilize the major greenhouse gas carbon dioxide. Besides, the thermal stability of the copolymer resulted from CO_2 and CHO was also found to be better than that of the copolymer from CO_2 and PO via a comparison of T_g and T_{10} . These results indicate that not only a high yield and a high molecular weight of the copolymer can be obtained, but also the thermal properties can be adjusted as desired by a proper choice of an epoxide or a combination of epoxides in a copolymerization reaction with CO_2 .

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Table 1 Comparison between the present invention and Stevens '415

	Stevens '415)	The present invention
The structure of copolymers	<p>The repeating polyethylene oxide units — (CH₂-CH₂-O) — may vary in length (Column 1, line 55)</p> <p>From 2 to 10 moles of 1,2-epoxide per mole of carbon dioxide are consumed in the formation of high molecular weight polycarbonate (Column 1, line 41).</p> <p>In the examples, the degree of carbon dioxide fixation of CO₂ is 12-13%.</p>	<p>"the content of alternative sequence structure exceeds 97%" (page 5, line 11)</p> <p>The degree of carbon dioxide fixation of CO₂ is above 42 wt% (page 5, line 11).</p> <p>The ratio of alkylene carbonate to CO₂ is approximal to 1/1.</p>
Catalyst system	"Base catalysis" (column 1, line 26), which is a typical anionic polymeric catalyst	The catalyst consists of a rare-earth coordination compound, an alkyl metal compound, a polyol and a cyclic carbonate (page 2, line 3 from the bottom). It is an anionic coordination catalyst.
Solubility in methanol	Soluble in methanol. This kind of polycarbonate is called as block polyether-ester.	Insoluble in methanol and ethanol, and only soluble in methane chloride, chloroform, acetone, tetrahydrofuran, and the like.
Molecular weight	700-5000 (column 1, line 21)	> 30,000 (page 5, line 10)
Reaction temperature	100-250°C (col. 2, line 48)	60-100 °C (page 4, line 3 from the bottom)
Color and state	"light to dark amber" (column 1, line 72), viscous liquid	White, solid powder
applications	"By virtue of their reactive terminal hydroxyl groups, they may be reacted with polycarboxylic acids such as phthalic, maleic, succinic, fumaric and adipic among others to obtain alkyd type resins which are useful as laminating resins, molding resins, coating compositions for metal, wood and woven fibrous products such as silk, cotton wool and rayon. These polycarbonates are reactive with isocyanates yielding urethane." (column 7, lines 46-54)	As a polymer having definite Tg, the present polycarbonate can be directly used as a structure material without previously reacting with other organic materials.

Table 2 Comparison between Tan's article and the present application

	Tan	The present application
The number of components	3-parts catalyst system: rare earth coordination compound-ZnEt ₂ -glycerol	4-parts catalyst system: rare earth coordination compound-ZnEt ₂ -glycerol-propylene carbonate (or ethylene carbonate)
Catalyst activity	Under the best conditions, the highest catalyst activity for the copolymerization of PO and CO ₂ is only 4200 g polymer/mol Y	The catalyst activity for the copolymerization of PO and CO ₂ can be as high as <u>above 8000 g polymer/mol Y</u> , even the lowest activity (in examples) is also <u>above 4600 g polymer/mol Y</u>
Rare earth coordination compound	CF ₃ COO ⁻ , P ₂ O ₄ ²⁻ , CH ₃ COO ⁻ (1997); CF ₃ COO ⁻ , CH ₃ COO ⁻ , CH ₃ COCH=CO-CH ₃ , CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)COO ⁻ , NO ₃ ⁻ (2000)	Carboxylic acid group other than trifluoroacetic or sulfonic acid group with Ka values above 10 ⁻³ , such as, CCl ₃ COO ⁻ , CH ₂ Cl ₂ COO ⁻ , CH ₂ ClCOO ⁻ , o-chlorobenzoic acid group, α-tartaric acid group, benzene sulfonic acid group, naphthalene sulfonic group and mixture of one of more of them.
Solvent for copolymerization	The best solvent is 1,3-dioxolane (4200 g polymer/mol Y), DMSO and n-hexane is the worst solvent (trace polymer/mole Y)	The catalyst can be used to copolymerize PO and CO ₂ without using any solvent. Thus, the present copolymerization can be called as "polymerization-without-solvent"
Applicability	Solvent(s) is required in the polymerization and thus a recovery process is required.	The recovery process can be omitted.